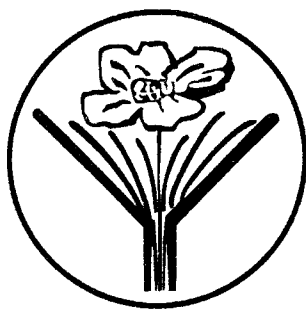


Vinogradov Society of Rheology
Russian Academy of Sciences
A.V.Topchiev Institute of Petrochemical Synthesis
University of Klaipeda

XIX SYMPOSIUM ON RHEOLOGY

COLLECTION OF ABSTRACTS



June 22 – 27, 1998
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В сборнике помещены тезисы докладов 19-го Симпозиума по реологии, организованного Реологическим Обществом им. Г.В.Виноградова, Институтом нефтехимического синтеза Российской Академии наук и Университетом Клайпеды. Тематика докладов охватывает широкий круг актуальных проблем реологии полимеров, дисперсных и биомедицинских систем, а также вопросы сверхпластичности металлов и керамик.

Сборник представляет интерес как для научных работников, так и для исследователей, занимающихся прикладными аспектами реологии: врачей-практиков, инженерно-технического персонала, связанного с переработкой и формированием полимерных материалов, композитов, металлов, и др.

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The collection of Abstracts of 19th Symposium on Rheology, organized by Vinogradov Society of Rheology, Institute of Petrochemical Synthesis of Russian Academy of Science and University of Klaipeda, comprehends the extended set of actual problems of rheology of polymers, dispersed and biomedical systems, as well as of superplasticity of metals and ceramics.

This collection may be interesting as for academical scientists, as for researchers dealing with applied aspects of rheology: doctors of medicine and engineers involved to processing and forming of polymers, composites, metals, etc.

Editor-in-chief,
Professor

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1998

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TEMPERATURE EVOLUTION OF STRUCTURE AND RHEOLOGICAL PROPERTIES OF LIQUID CRYSTAL COPOLYESTERS

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Rheological properties and phase transition in four-component copolyester (CPE) containing 40 mol % PET, 20 mol % (each) hydroxybenzoic, terephthalic acids and hydroquinone were studied in a temperature range 30-350°C by means of capillary viscosimetry, X-ray scattering (SAX and WAX) and DSC.

Peculiarities of flow curves of CPE are following: existence of two temperature regions (240-270 and 290-310°C) with various shape of flow curves; different values of effective activation energy in the low and high temperature regions (67 and 164 kJ/mol respectively); a dependence of viscosity on residence time at 240°C and its absence at higher temperatures; an influence of wall effect (slipping) on flow process of CPE at low temperatures and real flow of melts in a high temperature region.

The results obtained from rheological measurements were supplemented by structural investigations. The initial CPE is characterizing by absence of a long period structure. It has two phases; a crystalline one and a frozen smectic phase. At layer boundaries in a plane perpendicular to chain axis only weak ordering exists, but along fiber axis a prominent periodicity takes place.

At specimen heating in a temperature range 30-170°C an increase of CPE structure, perfectness was observed accompanying by increase of intensity (I) of initial reflexes and appearance of new ones in both meridional and equatorial planes. Degree of CPE crystallinity (D_c) also increases, although size of crystallites (L) remains invariable. At the temperature 170°C simultaneously with increasing intensity of diffuse dispersion (I_d) in a SAX image a new reflex appears at angle 25 min., that corresponds to a long period dimension $d \sim 200$ Å.

In a temperature range 170-220°C I of crystalline reflexes, D_c and transverse correlation length (ξ_L) noticeably decrease. But at constancy of longitudinal dimensions of crystallites their transverse dimensions increase from 65 to 75 Å. At 200°C d reduces to 180 Å and at higher temperature reflex on SAX disappears and in subsequent cycles heating-cooling was not observed. On DSC-traces an endothermic peak with enthalpy of 8,1 J/g corresponds to the temperature 220°C. Presence of this peak apparently connected with unfreezing of smectic LC matrix. The remaining part of CPE represents solid crystalline phase melting at 293°C. This phase plays the role of net junctions which prevent the actual flow of soften CPE. Therefore, in a temperature range 240-250°C a pure slipping, at temperatures 255-280°C superposition of slipping and flow and only at $T > 290^\circ\text{C}$ a real flow of CPE proceeds.

RHEOLOGICAL PROPERTIES OF LIGNIN- SILICATE COMPOUNDS

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The goal of this work is the formulating of gelation compositions on the basis of waste lignins, measurements of their rheological parameters and curves of flow as well as the elaboration of ways to control rheological behavior by varying pH of media, temperatures of gelation and electrolytes additives.

Waste-lignins become in enormous amounts from paper-producing industry. Utilization of these components will allow to reduce the possibility of an environmental pollution and is of interest to solve specific problems of different industrial branches, in particular, for oil recovery. Compounds of waste-lignins with sodium metasilicates seems to be perspective for oil recovery to align the permeability of oil pools.

Different kinds of waste-lignins were used to obtain gel-forming compounds with sodium metasilicates and other additives. Rheological parameters of these compositions were investigated using visco-rheometer at load with the constant rates of deformation within $16-1312 \text{ s}^{-1}$.

Mixtures of alkali solutions of lignins and sodium meta-silicates revealed reinforced gelation with lag-periods depending on concentrations of components and their ratio account for 5-20 min at 20°C . Systems are characterized by improved viscosity, strength, plasticity and thixotropy with resetting of mechanical properties after the failure of structures.

The treatment of systems at different temperatures within the range of $20-80^\circ \text{C}$ shown the essential growing of rheological parameters and reducing of lag-periods of gelation with the increase of temperature.

Gelation of compositions under various degrees of mineralization of water-pools negatively affects on the plasticity and strength of gels. Solutions of salts of alkali or alkali-earth metals were used as models of water-pools. To reduce the negative influence of the mineralization on rheological properties of gels polyacrylamide in quantities of 0.05-0.1 mass% was added in the compositions. This leads to an elimination of undesirable effects of electrolytes with viscosity and plasticity of systems were essentially increased under static as well as near oil-pool conditions. Evidently, macromolecules of polyacrylamide form structures with precipitates of alkali and alkali-earth metals hydroxydes, which are tolerant under conditions of the pool filtration.

A Three-Dimensional Polymer Composite Filled With Thermoplastic Particles

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The composite consists of an epoxy resin solidified in normal conditions and particles ($d \leq 2 \mu\text{m}$) of emulsion polyvinyl chloride (PVC), its pores filled with dioctylphthalate (DOF) as a plasticizer. The amount of the plasticizer reaches 40 % of weight in the PVC. DOF and PVC are well compatible. The particles swell at between 50 and 60°C , a sudden increase of volume is observed in heating the composite. Changes in its deformation properties are observed.

Thermal expansion factor of the composite at temperatures over $T > 60^\circ \text{C}$ changes slowly ($1.6-1.9 \cdot 10^{-4} \text{ 1/deg}$) in a wide range of ϕ (0-0.4) because of the specific properties of the particles, and is smaller, than predicted by the additivistic equation.

In the presence of dioctylphthalate CO groups, an inter-phase layer appears between PVC and the epoxy resin. The interlayer affects the deformation behaviour of the composite, when the PVC fillings level is $\phi \geq 0.25$. With $\phi < 0.25$ deformation refers mainly to the matrix.

The Budiansky model gives a better prediction of the deformation properties of the composite, as compared to the Kerner model.

Thanks to the thermoplastic filling particles in the range of $\phi \approx 0.20-0.25$, adhesion strength of the glue links (after thermal treatment) is increased about twice.

THERMOTROPIC LC MAIN-CHAIN COPOLYESTERS. Structure, Phase Composition and Temperature Behaviour

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Here we report the results of the DSC and X-ray scattering study in a wide temperature range of oriented samples of several families of rigid-chain wholly aromatic LC copolyesters with different chemical compositions. It was found that on heating of as-spun fibers above glass transition temperature the crystallization takes place in spite of irregular structure of macromolecules in random copolyesters. If the copolymer contains a monomer with a bulky side substituent, two crystalline phases are developed indicating the phase separation process associated with configuration isomerism because of possible head-to-head and head-to tail additions during synthesis. Upon heating, both modifications are transformed into mesophase states exhibiting the reversible transition of orthorhombic crystals into pseudohexagonal mesophases. It was also found that structure of the as-spun fibers of the copolyesters with different monomer units of equal length might be identified as the typical LC smectic S_A , whereas the copolymers containing monomer units which differ in length, in contrast to the first ones are characterised by the unusual aperiodic smectic mesophase. This LC state was identified as non-periodic layer structure, where the short-range order only is observed within the aperiodic layers oriented perpendicularly to the chain direction. This mesophase seems to be a mesomorphic state of novel generation. As far as we know, nobody still observed such a type of mesomorphic structures for the non-crystalline phase component of semicrystalline polymers.

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PHENOMENOLOGICAL DESCRIPTION FOR PROCESS OF MULTIPLE DISINTEGRATION OF SOLIDS UNDER THE INTENSIVE STRESS ACTION SUCH AS COMPRESSION & SHEAR

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A theoretical phenomenological model describing the process of multiple disintegration of solids under the intensive stress action such as compression & shear as a critical phenomena is proposed. The model assumed that due to this action some locally stress regions within the bulk of the material appear, inducing formation of defects in the network of physical or chemical links that provides a completeness of a specimen as a whole. The formation of the defects brings about the relaxation of the local stress in the matrix (i.e., about the plastic deformation of the sample) and, owing to this the next defect appears in another point. In consequence a totality of microscopic defects accumulates and, as their concentration attains some critical value, the completeness of the substance is disturbed and the multiple disintegration of a specimen occurs.

To describe the kinetics of process, the following set of equations was introduced:

$$\dot{u} = k_T + \sigma k_1 \frac{w}{1-w} (1-u) - k_2 u \theta(u_{cr} - u), \quad (1)$$

$$\dot{w} = \sigma k_3 (1-u)(1-w) - k_4 u w, \quad (2)$$

$$\dot{T} = k_5 u w - k_6 (T - T_{env}), \quad (3)$$

where u and w denote the volume fractions of microdefects and local stressed regions, accordingly ($0 \leq u, w \leq 1$); $\sigma = \kappa F \theta(u_{cr} - u)$ is the stress value caused by the external force F ; function $\theta(x_0 - x) = 1$ at $x \ll x_0$, $\theta(x_0 - x) = \varepsilon \ll 1$ at $x \ll x_0$, and in the narrow transition region at $x \propto x_0$ the function $\theta(x_0 - x)$ changes smoothly from 1 to ε ; $k_T = k_T(T)$ and $k_1 = k_1(T)$ are the rate constants for the spontaneous microdefects appearance and that induced by the external action; $k_2 = k_2(T)$ is the rate constant for "healing" of defects, the expressions $k_T(T)/k_1(T) = k_{T0} + \delta_T (\theta(T_{melt} - T) - \varepsilon)/(1 - \varepsilon)$ and $k_2(T)/k_1(T) = \exp(\Delta E/T)$ being valid in view of the above considerations (here and later on the temperature is given in energy arbitrary units); k_3, k_4 are the rate constants of the nucleation and relaxation of the local stressed regions, k_3 having only a weak dependence on the temperature, and this dependence can be neglected, whereas $k_4 = k_4(T)$ increases with the temperature by the exponential law ($k_4(T) = k_{relax} T$), as the relaxation processes in polymeric systems are limited by the polymer chains mobility; k_5, k_6 are the temperature-independent rate constant for the specimen's heating at the account of relaxation of local stressed regions, and the heat transfer coefficient of system to the environment, its temperature being equal T_{env} .

The analyses of steady-states of the set of equations (1) – (3) shows that a bistability in this system is possible. This fact allows to assume that the process of the multiple disintegration of a material occurs as the result of the jumping to the another branch of the steady-states in which the system is close to the collapse state.

MODELS FOR FORMATION OF SUPERMOLECULAR OLIGOMERIC LIQUID STRUCTURES. THEORY AND EXPERIMENT.

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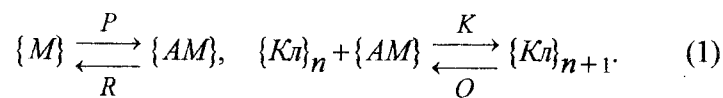
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The existence of supermolecular associations of various structure (associates, sibotaxies, etc.) in oligomeric liquids is widely used for interpretation of multiple features in rheological, relaxation, diffusion, sorption and other dynamic and stationary macroscopic properties.

This study offers some (from multiple possible) phenomenological quantitative theoretical models describing the relaxation kinetics for oligomeric systems and compares them to rheological and relaxation experimental data. These theoretical phenomenological models of the oligomer supermolecular structure formation are based on the following assumptions:

- the liquid system consists of the molecules which are incorporated within associates, and of "disorganized" molecules (which are not incorporated within associates);
- to attain thermodynamic equilibrium distribution by associates number and sizes which is independent on the initial conditions, the system should previously overcome some energy barrier which is determined by the nature of the components;
- activation of molecules allowing them to join to associates occurs due to thermal or mechanical (deformation) energy "injection" into the system from outside;
- the number of associates is invariable in the process.
- on the way to the equilibrium the associates sizes distribution created in the system after the external effect ceasing varies both due to the addition of separate activated molecules to the associates, and due to the cleavage of the molecules from associates;
- the number of associates in the process does not vary, i.e., the generation of new associates and disintegration of large associates into smaller ones does not occur. A separate activated molecule cannot be a nucleus of a new associate, but it can only join existing associates.

The following kinetic scheme of aggregation processes was used:



The analysis of the set of kinetic equations corresponding to the assumptions marked above shows, that within the framework of offered models it is possible to explain some anomalous experimental data. For example, the peculiarities of aggregation processes bring about the fact that two characteristic time scales are present in the oligomeric system; due to the processes of the molecules redistribution between associates the characteristic relaxation time can be very large for liquid system (reaching several day); it is possible also to give qualitative explanation of a temperature hysteresis of viscosity of oligomer which is based on the uncommon mechanism of bistability without the jumping-like changing of the system state.

The Poiseuille Flow of the Oldroyd fluid

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This work considers the precise solution to the problem modelling the Poiseuille flow of the Oldroyd viscoelastic fluid in a plane split. Unlike the known results, in this research we have obtained the explicit dependences of the rate and stresses on the transverse coordinate.

The Oldroyd equation which has the most general associated derivative keeping the symmetry [1] is written as

$$\begin{aligned} \tau + \lambda_1 \left[\frac{d\tau}{dt} - \tilde{w} \cdot \tau + \tau \cdot \tilde{w} + a(\tau \cdot \tilde{e} + \tilde{e} \cdot \tau) + b(\tau \cdot \tilde{e}) + c \tilde{e} \text{tr}(\tau) \right] = \\ = 2\mu \left[\tilde{e} + \lambda_2 \left(\frac{d\tilde{e}}{dt} - \tilde{w} \cdot \tilde{e} + \tilde{e} \cdot \tilde{w} + 2a(\tilde{e} \cdot \tilde{e}) + b(\tilde{e} \cdot \tilde{e}) \tilde{I} \right) \right] \end{aligned} \quad (1)$$

After inserting the dimensional parameters $\varepsilon = \frac{\lambda_2}{\lambda_1}$ and $A = \sqrt{1 - (a+b)(a+c)}$, and the

variables $q = \lambda_1 \frac{dv_z}{dx} A$ and $G = \frac{2R\lambda_1 A}{\mu}$, the integration of the equation of motion gives [2]

$$2q \frac{1 + \varepsilon q^2}{1 + q^2} = -G x \quad (2)$$

Equation (2) can be integrated to obtain an analytical expression for the longitudinal velocity in a parametric form

$$x = \frac{2q(1 + \varepsilon q^2)}{1 + q^2} \frac{1}{G} \quad (3)$$

$$v_z = \left\{ -\varepsilon(1 + q^2) + (1 - \varepsilon) \left[\ln|1 + q^2| + \frac{2}{1 + q^2} \right] + C \right\} \frac{1}{G} \quad (4)$$

The arbitrary constant C is defined from the boundary condition $v_z = 0$ at $x = \pm 1$.

For the Oldroyd model at $\varepsilon < \frac{1}{9}$, the velocity profiles and flow curves show the closed

loops. The existence of the solution for different sets of parameters of rheological model is analyzed.

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Pressure Dependent Viscosity Fluid Flow

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In this study a stationary plane-parallel pursuer-driven fluid flow is considered in a plane channel with one wall fixed and the other moving at the prescribed velocity (including zero velocity as a special case). The channel walls are assumed to satisfy the non-slip conditions.

In this case the governing equations are reduced to

$$\frac{\partial p}{\partial z} = \frac{\partial}{\partial x} \left(\mu \frac{\partial v_z}{\partial x} \right) = \frac{\partial \mu}{\partial x} \frac{\partial v_z}{\partial x} + \mu \frac{\partial^2 v_z}{\partial x^2}; \quad 1.$$

$$\frac{\partial p}{\partial x} = \frac{\partial}{\partial z} \left(\mu \frac{\partial v_z}{\partial x} \right) = \frac{\partial \mu}{\partial z} \frac{\partial v_z}{\partial x}; \quad 2.$$

$$\nabla \cdot \mathbf{v} = 0 \quad 3.$$

The viscosity is related to pressure by equation

$$\mu = \mu_0 (1 + \alpha(P - P_0)), \quad 4.$$

which is the first term of the Barus law expansion in a Taylor series commonly used in the lubrication theory.

From equations (1), (2) it follows that

$$\frac{\partial^2 p}{\partial x^2} = \frac{\partial^2 p}{\partial z^2}. \quad 5.$$

The solution is found in the form $v_z = w(x)$, $p = A_1 + A_2 g(x) \cdot e^{-kz}$.

Pressure distribution with respect to x is defined by differential equation of the second order

$$\frac{d^2 g}{dx^2} = -k^2 g, \quad 6.$$

whose general solution is

$$g = C_1 \operatorname{ch}(kx) + C_2 \operatorname{sh}(kx) \quad 7.$$

In the case when one of the walls moves with velocity w_0 the pressure distribution in the channel is defined by

$$p(x, z) = p_0 - \frac{1}{\alpha} + \frac{1}{\alpha} \left[\operatorname{ch}(kx) + \operatorname{sh}(kx) \frac{e - \operatorname{ch}(kH)}{\operatorname{sh}(kH)} \right] e^{-kz}, \quad 8.$$

and the profiles of relative velocities take the form

$$\frac{w}{w_0} = \ln e \frac{g_0}{g} = -\ln \left[\frac{1}{e} \left\{ \operatorname{ch}(kx) + \operatorname{sh}(kx) \cdot \left(\frac{e - \operatorname{ch}(kH)}{\operatorname{sh}(kH)} \right) \right\} \right] \quad 9.$$

under the requirement that $\mu_0 \alpha k w_0 = \pm 1$.

From equations (8) and (9) it is readily seen that the pressure across the channel thickness is essentially inhomogeneous. At high pressure drops the pressure at the channel walls is essentially higher than in the center and with increase of the pressure drop the velocity profile changes from a parabolic to a conical type. The flow curve shows a flow rate saturation.

Investigation of Structure Mechanical Properties of Flour-Water Suspension

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Changes in viscosity of flour - water suspension during gelatinization is considered one of main structure-mechanical properties of the system characterization bread making procedure technological parameters, equipment working regimes and finally the quality of products. Apparent viscosity in non-Newtonian systems, including flour-water suspension, is dependent on many factors - deformation rate (rate gradient), temperature, suspension concentration, temperature-time history and other factors.

The aim of the present work is to establish mathematical relationship between apparent viscosity and possible technological factors and to choose the mathematical model which fully describes the character of this relationship.

The dependence of flour-water suspension on various technological parameters was established according the principles of the theory of resemblance - all experiments were carried out under similar conditions, allowing to find the dependence of apparent viscosity of each parameter. All measurements were made using viscosimeter "Reotest-2", system S/S₃.

In the present investigation was used ground winter wheat Alba and Sirvinta cultivated in Lithuania.

The results of the investigation of the relationship between apparent viscosity and technological parameters (rate gradient, water content, temperature, changes in T-t history) lead to the conclusion, that the established relationships and constants allows to calculate analytically apparent viscosity and to model the technological procedure.

In order to collect a complex data about flour baking properties it is necessary to investigate all wheat cultivated in Lithuania according the described method

The rheological properties of mesophase polydiethylsiloxanes in bulk and monolayers.¹

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Linear polysiloxanes are capable of forming mesophase under certain conditions. The rheological properties of mesophase for such substances are investigated insufficiently at the moment. Polysiloxanes also have unusual properties in monomolecular layers formed on the "water - air" interface. It has been found that compression of PDMS monolayer occurs through transformation to bilayer in helical conformation. Cyclic polysiloxanes (CPS) form discrete multilayer structure on compression of monolayer. The thickness of following layers ratio for thickness of a monolayer, as 2/1, 3/1, 4/1 ... It has been shown, that this phenomenon is closely related with mesophase behavior and rheological properties of CPS.

The second member of homological row of polysiloxanes (PDES) is capable of forming of the column type mesophase. At same time, PDES does not form monomolecular film on the surface of clean water. It is connected with intramolecular energetic rotational barrier, which does not allow to get necessary conformation of the chain, allowing to form monolayer. However, in the case of preparation of the monolayer from a solution of a mixture of PDMS and PDES, the PDES monolayer will be formed. This monolayer lays on the PDMS monolayer. This method allows to obtain the PDES monolayer and to study its rheological properties.

In this report the rheological properties of PDES in bulk, obtained by means of rotational rheometer are discussed and compared with the rheological properties of monolayers, obtained by means of surface capillary rheometer on the PDMS substrate. It has been found, that monolayer behaves as typical Bingham plastic body, with yield point in the region of mesophase. It has been observed the difference in the surface and bulk viscosity values.

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VISCOSITY OF CELLULOSE/ LIQUID CRYSTAL POLYESTER BLENDS IN N-METHYLMORPHOLINE-N-OXIDE SOLUTIONS.

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It is widely known that adding of liquid-crystal polymers (LCP) to high-viscosity thermoplastics leads to significant drop in blends viscosity, which improves their processing and can also results in enhanced material properties.

Therefore it would be especially interesting to investigate of LCP introducing on rheological properties of cellulose solutions in N-methylmorpholine-N-oxide (NMMO), that were investigated earlier. For this purpose thermotropic alkylene-aromatic polyester polydecamethylene-terephthaloylbenzoate (PDTOB) was chosen (mesophase existence temperatures 160-185°C), which dissolves in NMMO without lyotropic mesophase formation.

Solutions with concentration of both polymers 20% were investigated in temperature range 90-120°C. Flow curves were obtained using capillary and rotational rheometers, and zero-shear viscosity and flow activation energy values were calculated.

Viscosity of solutions containing two polymer components is lower than that of cellulose solutions in NMMO at any components ratio. At PDTOB content in solution 4% the viscosity decreases three times. Generally, the positive deviation from additive dependence "viscosity-composition" takes place.

Mechanical properties of solid extrudates (after removing NMMO water) are the best for PDTOB content ~ 2% (total concentration of both polymers in solution is 20%). Namely for this composition the fibrillas morphology of LC phase was observed.

AN INFLUENCE OF COMPATIBILITY AND COMPONENTS PHASE STATE ON RHEOLOGICAL PROPERTIES OF POLYPHOSPHAZENE BLENDS.

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A systematic research of influence of compatibility and phase state of components on rheological properties of poly-(bis)-trifluoroethoxyphosphazene (PTFEP) and its copolymers blends have been done.

Three copolymers prepared by substitution of short trifluoroethoxy sidegroups in PTFEP on 5; 7,5 and 10 mol.% of dodecafluoroheptoxy groups (DDFH). This procedure leads to essential decrease of mesophase region existence in copolymers, up to its total disappearance.

Two temperature ranges have been investigated. In the first case (temperature is 250° C) both components exist in isotropic melt state; in the second one - at 225° C PTFEP is in meso-phase state and copolymers are in isotropic melt.

The compatibility of components in blends at small content of copolymer by DSC and microinterference methods was estimated. The region of compatibility decreases with increasing concentration of DDFH-groups in copolymer. This fact is confirmed by data of rheological experiments, namely by "viscosity - composition" and "spurt stress - composition" dependencies. Both spurt stress and viscosity can be used as criteria of compatibility in blends of isotropic components.

Much more complicated rheological behavior of the blends was observed at 225° C. The shape of flow curves sharply changes from viscoplastic to non-Newtonian depending on concentration of mesophase PTFEP. The blends have a yield point for composition where PTFEP is a matrix. But when phase inversion takes place and an isotropic copolymer becomes a matrix, the yield point disappears and flow curve has a shape inherent for non-Newtonian liquids. In some cases (at components ratio 1:1) the flow with both yield point and "spurt" was observed. At the same content of DDFH-groups in isotropic blends and neat components have a similar level of viscosity anomaly, but if components are in different phase state the blends appear much more non-Newtonian behavior compared with copolymers.

Alternative theory of hydrodynamic shielding effects in flowing polymer solutions

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The hydrodynamic shielding (hydrodynamic interactions) effects largely determine rheological properties of dilute polymer solutions. The existing theory of hydrodynamic shielding (HS) was developed by analogy with the theory of hydrodynamic interactions in hard sphere suspensions. Both these theories meet with tremendous mathematical difficulties, which force to introduce uncontrollable approximations.

Here we propose a new approach based on a two-fluid model. This model pictures a flexible polymer coil as a mixture of two fluids, formed by solvent molecules and segments of a chain macromolecule. Microstates of the model are specified by coarse-grained space distributions of segments, as in the existing theories, and by flow velocity fields of segments and solvent. In the approach proposed the HS arise from an intercomponent friction forces which are proportional to the differences of segment and solvent flow velocities.

Different versions of two-fluid model are possible. The most simple version is based on a mean-field approximation for the segment connectivity. The kinetic equations of this minimal two-fluid model are the equations for fluid mixture hydrodynamics in an external field. A counterpart of the minimal two-fluid model in the existing theories is a dumbbell model.

The linear rheological properties of dilute polymer solutions: the diffusion coefficient and intrinsic viscosity, as well as nonlinear ones, that are the normal stress differences (NSD) in simple steady shearing flow, were calculated using the minimal two-fluid model. The results obtained describe the HS effects in qualitative agreement with experiments and more accurately than existing theories based on the dumbbell model. It must be stressed particularly that our approach predicts in agreement with experiments the first NSD to be positive and the ratio of second to first NSD to be small negative quantity.

The results obtained in the frame of the minimal two-fluid model allow to believe that the alternative theory of the HS effects will play a significant role in the polymer solution rheology in the future.

Two-Fluid Multicomponent Model in Rheology of Dilute Polymer Solutions

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A new continuum model in dynamics of dilute polymer solutions have been introduced in works [1,2], in which a polymer coil is represented as a mixture of two liquids: solvent and segments of macromolecules (the minimum model). The two-fluid model (TFM) and the well-known bead-spring model differ mainly by the presentation of hydrodynamics interactions.

The study in the frame of statistical irreversible thermodynamics has shown that polymer liquid (PL) in TFM is a multicomponent one. The dynamics of the dilute multicomponent TFM is described by equation for solvent velocity field, perturbed by force from side of PL, by relations for this force and tensor of local stresses in PL, determined by reduced density of momentum flux, and the Rouse diffusion equation for slow variables, which describe a large scale movements in polymer coil. The minimum model is a special case of TFM, if PL is considered as one-component system.

In the first approximation correlations between the different components of PL are not taken into account. In this approximation the macromolecule diffusion coefficient and intrinsic viscosity are calculated as an example. The results of calculations are compared with experimental data. The theory developed can be applied in non-linear range of flows. It is possible to take into account correlations between different components of PL in the future.

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INFLUENCE OF SURFACTANT ON RHEOLOGICAL PROPERTIES OF GELATIN BILATERAL EMULSION AND FOAM FILMS

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The polypeptide gelatin has been used extensively in the photographic, food and other industries because of its usefulness as an emulsifier, peptizer, stabilizer and film-forming binder. Influence of low-molecular-mass surfactant (sodium dodecylsulphate, cetylpyridinium chloride) on stability and rheological properties of the bilateral thin emulsion and foam films has been studied.

When surfactants are added to aqueous gelatin solutions, binding of surfactants by gelatin with complex formation in consequence of electrostatic and hydrophobic interactions takes place. The properties of these complexes are not additive to individual components ones. They are determined by a binding degree of surfactant by gelatin. At the certain ratio of components these complexes are surface-active more than macromolecules of gelatin.

The work has been aimed to study stabilizing ability of the gelatin-surfactant complexes on the model systems: thin bilateral foam and emulsion films (elements of foam and emulsion). The range of surfactant-gelatin ratio (complex composition) and pH values were found when the stable foam and emulsion film are formed. Rheological properties (yield shearing stress, viscosity) of films were measured on a surface elastoviscometer using the method of progressively increased load and attenuated oscillation.

It was shown that the thin bilateral films stabilized by gelatin-surfactant complex give synergism of the rheological parameters when the surfactant concentration is less than the maximum amount bound by gelatin. The rheological properties of foam and emulsion films are extreme at the isoelectric condition of complex at pH 3,1. Decrease of rheological parameters of the emulsion films at the surface with organic liquid (decane, heptane) in comparison with foam films at the surface with air has been explained by solubilization of hydrocarbon adjoining with aqueous phase by hydrophobic zones of the gelatin-surfactant complex.

Under such conditions interface adsorption layers (elements of thin foam) of gelatin and its mixtures with surfactant at the solution/air and solution/organic liquid interfaces were investigated. Rheological parameters were measured by the method of progressively increased load and rotating the disk at a constant deformation rate. The thicknesses of the layers were measured by a method of IR spectroscopy.

At the specific ratio of components in the range of the stable film formation the layers are characterized by high values of the rheological parameters. Simultaneously there is a plateau in the surface and interface tension isotherms made by Wilgelme method, which indicates the saturation of the surface by the surface-active gelatin-surfactant complexes. Increasing strength of stabilizing layers formed by complexes in comparison with gelatin ones is accompanied by decrease of the layer thickness. This is connected with conformational changes of gelatin macromolecules interesting in complex with surfactant in adsorption layer.

The gelatin-surfactant complexes are good stabilizers of the bilateral foam and emulsion films and the particular rheological parameters of films correlate with foam and emulsion stability. This is caused by increasing role of structural-mechanical barrier as a result of formation of strengthened adsorbed layers.

STATE EQUATIONS OF IDEAL AND REAL ELASTOMERS

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Among all known elastomer state equations only one is proved quite exactly from the point of view of mechanics that is Rivlin equation [1]

$$W=C(\lambda_1^2+\lambda_2^2+\lambda_3^2-3) \quad (1)$$

where W is deformation energy density, λ_i - main axes elongations.

All the rest equations are postulated basing on various concepts.

Portion one of this article offers an exact proving of the state equation of incompressible elastomer under condition of its constant isotropy in a state of deformation. It is shown that the only equation satisfies this condition

$$W=C(\lambda_1+\lambda_2+\lambda_3-3) \quad (2)$$

which, as well as (1), is particular case of the potentials of a more general case.

One can call materials obeying (1) and (2) rules as ideal, opposite to real bodies.

Relations (1) and (2) describe behavior of unfilled elastomers under not large deformations quite well. Relations (1) is closer to the experiment with bulged nets, (2) is closer to 'dry' ones.

Concerning rubbers containing active filler of technical carbon, relations (1) and (2) describe their behaviour outstandingly bad under little and middle deformations which are appropriate for working of practically all elastomer goods. Despite many attempts, it is not possible to acknowledge the solving problem of optimal state equation of a filled elastomer as closed at the present time. One of the important causes of it is absence of simple and reliable experimental methods of definition of rubber mechanical qualities in spontaneous complex strained deformed state.

Portion two of the article puts forward a method of constructing state equations, the last ones having good concordance with experiment when minimal number of constants. The method is based on selection of the appropriate expression for deformational dependence between elastomer module and its following integrating in invariance from.

Experimental method description is given, including fresh ones, qualified to transfer the problem of optimal state equations constructing out of the sphere of art into the sphere of common work.

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ADHESIVE STRENGTH OF CARBON FIBER - POLYMER JOINTS AT VARIOUS LOADING RATES.

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The behavior of polymer/fiber interface under various loading conditions is one of the important aspects of composite rheology. However research of this problem is not as abundant. Especially it is the case for the joints in which very thin and brittle carbon fibers are used as adherent. In this work we tried to fill this gap. The pull-out technique was exploited for measurements of the shear adhesive strength between carbon fibers of diameter 7 μm and polymers. The methods of specimen preparation were developed of such fibers with various adhesives. The joints of typical thermosetting (epoxy) and linear thermostable (poly(arylene sulphone)) polymers were tested at loading rates differing by many orders of magnitude. It was found that the relationships between τ and loading rate for both thermoreactive and thermoplastic polymers are the same. The τ value is linear function of logarithm of stress growth rate $\dot{\tau}$:

$$\tau = C_1 + C_2 \log \dot{\tau} \quad (1)$$

The constant C_2 characterizes the relaxation behavior of the interface. The values of C_2 found to be controlled primarily by the chemical nature of the adhesives. It follows from the comparison of the present data with the results obtained earlier by the study of adhesion of polymers under investigation to the another fibers.

Equation (1) allows also to presume the validity of the thermofluctuation mechanism for adhesion fracture and to use Zhurkov equation for the calculation of joints durability. The data obtained can be also used to elucidate the influence of the fiber/matrix interface on the composite properties, since the joints tested can be considered as elemental unit of fiber-reinforced materials.

CURE KINETICS BEHAVIOR AND PROPERTIES OF EPOXY-AMINE ADHESIVES .

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Epoxy resins based adhesives are widely used nowadays. In the present work characteristics of curing processes of epoxy-amine systems were studied.

The cure of epoxy-amine systems was studied by viscometry, dynamic mechanical analysis and differential scanning calorimetry. The temperature intervals both below and above the glass transition temperatures of completely cured composites were studied.

Time dependences of viscosity for curing compositions were found to be governed by exponential type equation: $\eta = \eta_0 e^{-kt}$. The temperature dependences of η and degree of conversion (β) were plotted, activation energies were found.

Time dependences of chemical conversion were described by first and second order kinetics. DMA and DSC don't give the same parameters of kinetic equations. Isothermal calorimetry doesn't show emission of heat of the reaction, while shear modulus and glass transition temperature are changing significantly. Time dependences of the degree of conversion were compared with adhesion strength and internal stresses of the compositions. Performance characteristics (strength, deformability, residual stresses) of end products depend on the technology of the cure and are directly related to kinetics of reactions and corresponding the evolution of rheology.

RHEOLOGY OF PHYSICAL NETWORKS

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The current descriptions of polymer rheological properties are based on the Rouse model in short time interval and the reptation model for large time. Because of strong dependence of terminal relaxation time on the chain molecular mass the reptation model leads to conclusion of autonomic behavior of polymer fraction: time and temperature of the terminal relaxation of the polymer chains are affected by their molecular mass only at any constitutions of the systems. At the same time the modern relaxation methodologies (NMR, infrared dichroism) show the reptation model has no quantitative (sometime qualitative) coincide with the theoretical conclusions.

The model of physical network being developed by authors at the last time allows to understand some experimental peculiarities, particularly, the mutual influence of macromolecules of different molecular mass (coupling effect): the relative increasing or decreasing of terminal relaxation times in the presence of macromolecules of larger or smaller molecular mass. Molecular mass distribution effect on the flow curve is explained on the base of this approach. The model of physical network allows to describe the wide circle of rheologic properties including the critical phenomena in the course of the flow of polymer melts and solutions at the high shift rate.

RHEOLOGICAL PROPERTIES OF INTERFACIAL LAYERS OF SERUM ALBUMINS IN THE PRESENCE OF ADDITIVES OF DIFFERENT NATURE

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Serum albumin (SA) is the main protein of blood as well as some vessel-out liquids. Aqueous solutions of SA at respect concentrations behave as newtonian liquids and are described by Einstein equation. In contrast with this interfacial adsorption layers of SA formed at interfaces at the same concentration of aqueous solution can be represented with rheological parameters respect to solids.

Lots of SA functions (binding and transport of substances, osmotic control, enzyme-like) are determined by details of structure of the SA molecule (M.m. 66000), which consists of three domains and can be regarded as a spheroid of $14 \times 4 \times 4$ nm. Total content of hydrophobic aminoacid residues is equal to 60% with the mean area of such residue of 1.28 nm^2 and the mean area of polar one of 0.3 nm^2 .

SA is a typical surface active substance and SA adsorption results in essential reducing of surface tension, but the role of surface phenomena for SA functions is not clear in details, in spite of a lot of indications of interfacial layers formation in vivo, for example, as protective coating films of a specific structure, which determine biocompatibility of blood with polymers for implantation reducing thrombogeneous properties of their surfaces.

Detailed investigations of SA interfacial layers at different interfaces allow to conclude, that SA adsorption leads to much higher surface concentration of protein in vicinity of a surface, of one order higher than SA concentration of equilibrium aqueous solution. The rise in concentration results in the formation of interfacial structures with properties of liquid crystals or coagulation dispersions. For these structures rheological parameters, such as modulus of elasticity, Shvedov's and Bingham's viscosities, limits of flow, critical shear stresses and periods of relaxation, have been accurately measured.

The special goal of work is the control rheological properties of SA interfacial layers by addition of lipids, electrolytes, glicans and nonpolar liquid phases. Modern methods of interfacial layers investigations were used, allowing to measure rheological parameters, isotherms of two-dimensional pressure, surface and interfacial tension. Isotherms of adsorption were recorded by means of radioactive indicators using tritium labelled SA and ATR spectroscopy in UR and UV regions. Sizes of SA associates in liquid phases at equilibrium have been measured by elastic light scattering method.

Added substances lead to a essential change of rheological parameters and character of flow of interfacial layers of SA formed at equilibrium between two immiscible liquids due to influence on lateral intermolecular interactions resulting in a transformation of two-dimension coagulation structures.

CHARACTERISTIC OF HAEMORHEOLOGICAL FACTORS IN HEALTHY MEN

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In 64 healthy men (age 39 - 64 years) were investigated following parameters of blood: haematocrit (Ht), fibrinogen (Fg), blood viscosity (BV), erythrocyte and platelet aggregation (EA, PA), erythrocyte deformability (ED), the content of prostanoids (PGA, PGE, PGF, TxB_2 , 6-keto PGF 1α), catecholamines (adrenaline, noradrenaline), parameters of lipid metabolism.

Matched correlative analysis reveals the relation between the main haemorheological parameters. A significant correlation was found between BV and Ht ($r = 0.698$, $p < 0.05$), Fg ($r = 0.465$, $p < 0.05$), ED ($r = 0.578$, $p < 0.0001$) and indices of lipid profile (total cholesterol (TC) and its fractions - triglyceride (TG), low - density lipoprotein (LDL), very low - density lipoprotein (VLDL).

Narrate interrelation was marked between PA and total cholesterol ($r = 0.490$, $p < 0.01$), LDL ($r = 0.473$, $p < 0.01$), atherogenic index (AI) ($r = 0.408$, $p < 0.01$).

A significant negative correlation was found between ED and TC, LDL, VLDL, AI and positive correlation - between ED and HDL. Positive correlation was revealed also between EA and PA ($r = 0.73$, $p < 0.01$) and direct correlation those parameters with concentration of adrenaline in the blood ($r = 0.450$, $r = 0.457$, $p < 0.05$). No correlatoin was found between concentration of some prostanoid series and blood cells aggregation but was revealed a significant negative correlation between PGE/PGF ratio parameters and PA induced by ADP ($r = -0.740$, $\delta < 0.02$) and by adrenaline ($r = -0.901$, $p < 0.02$).

Thus our data confirm interrelation between the main haemorheological parameters and indices of lipide profile, catecholamines and prostanoids in healthy subjects. These results indicate that investigated biochemical systems may play a role in the haemorheological regulation and platelet - vascular interactions.

Modification of rheological properties at various mechanisms of acute stroke

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77 patients were studied in dynamics of acute stroke, among which the I group made patients with atherothrombotic stroke (n=30), the II with cardiogenic stroke (n=22), the III with lacunary stroke (n=14), in IV (n=13) patients with the conditional diagnosis of hemorheological stroke were joined. There were analyzed the viscosity performances of blood (VB) at various velocities of a shift, calculated indexes of erythrocyt aggregation (IEA) and index of erythrocyt deformability (IED), aggregation activity of platelets; levels of hematocrit (Ht), fibrinogen (Fg), D-dimer (D-d); index of fibrinolysis (IF). In patients with atherothrombotic stroke the amplification of hemorheological activation developed against the background of a raise of viscosity of blood at all velocities of a shift, magnification IEA and drop IDE, at a raise of Ht. It is marked, that the enumerated modifications of hemorheology were kept in current of the whole acute phase of stroke. In group with cardiogenic stroke in the first days of disease on the first plan was advanced sharply expressed activation of hemostatic potential. In consequent terms of observations a diminution of hemostatic activation is marked, at preservation increased VB at low velocities of a shift with the tendency to formation of erythrocyt aggregates. In patients with lacunary stroke the hemorheological picture a little bit differs from the first group patients. The viscosity of blood at high velocities of a shift did not differ from normal values, but its raise is marked at low velocities of a shift. In IV group of patients the stroke developed on a hum noise of a raise of viscosity of blood at low velocities of a shift, essential magnification of Ht, EA, Fg, increased AT at an amplification of fibrinolysis and lack D-d. Submitted data have shown, that use of viscosimetry at various velocities of a shift has allowed to reveal distinction of hemorheological structure at various on the mechanism of development of acute stroke, and also to justify a possibility of development of stroke on a type of hemorheological microocclusion.

CERTAIN RISK FACTORS OF CEREBROVASCULAR DISORDERS AND RHEOLOGICAL PROPERTIES OF THE BLOOD IN HEALTHY MEN.

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64 healthy men (age 39 - 64 years) were studied. Evaluation of rheological indices was performed and included determination of blood viscosity (BV), haematocrit (Ht), erythrocyte and platelet aggregation (EA, PA), erythrocyte deformability (ED). Statistical method of quartil analysis was used to establish borders of normal investigated haemorheological parameters. Values appertained to the second and to the third quartils were considered as normal.

The aim of our study was to assess the impact of such risc factors of CVD as age and harmful customs (alcohol and cigarette smoking abuse) on the haemorheological characteristics in healthy subjects.

To examine age -related haemorheological changes the patients were subdivided in three groups (40 - 49 years, n = 26, 50 - 59 years, n = 30; 65 and older, n =6). Comparison conforming haemorheological indices in those groups showed that increasing age is associated with increased values of BV, Ht, PA and, especially, EA ($p < 0.01$).

To investigate the influence of harmful customs connected with risr of CVD development on the investigated rheological indices those parameters were compared in next subgroups : 1- patients without smoking custom, 2-patients smoking to 19 cigarettes per day, 3- patients smoking 20 and more cigarettes per day, 4-patients that not apply alcohol, 5-patients with friquent alcohol consumption. Analysis of data revealed negative influence of harmful customs on the blood cells functions. Friquent alcohol consumption was associated with significance increasing of EA($p < 0.01$); in patients smoking 20 and more cigarettes per day was marked tendency to effort of erythrocyte and platelet aggregation and increasing of Ht. . No association was found between smoking in smool dosage and investigated parameters.

To assess influence of permanent smoking abuse on the antiaggregation potential of the vessel wall we used the "cuff"-test. Results of this test showed the negative effect of this factor on the antiaggregation properties of the vessel wall in healthy men.

Thus our data confirm that healthy subjects older 50 years have tendency to decline haemorheological parameters, and the presence such risc factors of CVD as smoking and alhogol abuse contribute those changes. Therefore patogenetic effect of the smoking refers to blood cells functional condition and to the weakening of antiaggregation potential of the vessel wall.

Rheological Properties of Flocculants and Their Efficiency

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Modern chemical manufacturing requires an application of waste-free technologies including a waste recovery. With purpose to concentrate water suspended particles and to extract bioactive ingredients for wood antiseptic treatment waste recovery we suggested a technological process of natural coagulation and flocculation of small solid particles.

The efficiency of high-molecular flocculants is connected with the high molecular weight. These solutions have viscosity usually higher than that for low-molecular and colloid solutions of the same concentrations. In most cases in the flocculant solutions the viscosity anomaly caused by orientation of molecules along flow direction is observed.

For getting information about flexibility, volume, size and shape of polymer molecules of flocculant and about interaction between polymer and the solvent, we studied the intrinsic viscosity of diluted solutions in antiseptic process medium.

The macromolecules of flocculant represent flexible chains or globes. With increasing of molecular weight the molecules are able to higher bending. The functional groups led to changes of molecular charge thus the viscosity increases. It was found that the viscosity depends on pH of the process medium.

Using of rheological properties of flocculants at antiseptic treatment of wood wastes provides with primary products, improving of labour conditions and profit rise of wood processing plants. Simultaneously environment protection is greatly improved.

Influence of Rheological Properties of Beverages on Stabilization, Quality and Economical Efficiency

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For stabilization of beverages the direct action flocculants have been used recently. The efficiency of flocculant is connected with its molecular weight. We studied the influence of this characteristic on the technological process of wine manufacturing and quality of obtained industrial wine products. One of the flocculant characteristics for beverage stabilization is its intrinsic viscosity. The study of this parameter has shown that flocculant had high efficiency of defecation at treatment of wine materials and beverages in concentration 0,1 % or 20 mg/l in water. The structural studies has proved a filiform shape of the flocculant at this concentration. In acid medium the associates of dendrite shape were presented that ensures an active flocculation of particles.

For confirmation of cationic nature of the used flocculant the particles of negatively charged gold in hydrosol were introduced into the system. Thus we observed the fine particles of gold hydrosol being adsorbed on the surface of flocculant fibrils, that allowed increase in efficiency of its application.

It was also noticed that after 3 hours of contact the stum defecation is coming to the end and both the velocity of filtration and the yield are increased. As consequence of low crusting and instant flocculation of suspension while using dimethylaminomethylpolyacryamide the additional yield of wine materials and beverages was increased on 12%.

The proposed modifications of technological process has allowed to reduce a term of technological process on 11-18 of days.

RHEOLOGICAL BEHAVIOUR OF CARBONATE FILLED ELASTOMERIC ADHESIVE COMPOSITIONS

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The dependence of steady shear viscosity of polychloroprene adhesive compositions on carbonate type disperse fillers was investigated. The influences of variation in filler's particle size and weight fraction on rheological behaviour and on microstructure were studied. The average filler's particle size ranged in the broad interval - from 14.4 to >100 μm . The dispersions were prepared in the chloroprene rubber solution in organic solvents.

The particle's size distribution and solids weight fraction have strong rheological effect, which are probably related to changes in the microstructure of the dispersion. For fixed shear rate at low solids weight fraction the relative viscosity increase linearly with increase in the particle's diameter. In the case of the high filled coarse suspensions the viscosity significantly reduces due to the high particles sedimentation. Similar effect is observed in case of low particle diameter, which can be related to the large clusters formation. These clusters are responsible for the viscosity decreasing due to increase in settling properties. The suspensions with medium particle size show high viscosity properties in all cases of filling with no observable aggregation effect.

A direct relationship between the rheological properties (steady shear viscosity) and the carbonate filler nature was observed, also.

Rheology of Complex Polymeric Fluids

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Polymer melts and solutions themselves are complex rheological objects, since viscoelasticity, relaxation and time-dependent effects are inherent for them. But among polymeric systems there are specific ones with complex structure: lyotropic and thermotropic liquid crystal (LC) polymers, blends and dispersions containing particulate anisometric filler. All these systems appear anisotropic viscoelastic behavior initiated either by thermodynamically stipulated anisotropy of structure or flow-induced orientation of dispersed phase droplets or particles. Besides, interaction between phases in heterophase systems can lead to an additional, unpredictable a priori rheological response.

So, the main features of rheological behaviour of LC melts, polymer blends containing LC component and LCP filled by different fillers will be considered in this paper. As one can see from reenumeration of the objects under investigation namely LC matrix was used for all of them. In this case both levels of anisotropy exist: inherent to LC medium and induced as consequence of inclusions orientation at flow.

Such objects require the special equipment for measuring the anisotropic viscoelastic properties. Such instrument was designed and constructed in our work-shop allowing to realise on cylinder-cylinder geometry three kinds of deformation: rotation (steady shear) and oscillations in two orthogonal directions, as well as superposition of one mode of oscillation on steady-state shear [1]. The idea is that steady shear will initiate orientation of either LC domains, or droplets and particles and oscillation regimes will control this orientation. From this viewpoint the superposition regimes are the most interesting.

For pure LCP the expected results were obtained, namely dynamic moduli are lower at longitudinal superposition and higher for transversal one. For commodity thermoplastic melt (poly-4-methylpentene-1) storage and loss moduli decrease at both superposition regimes. It means that for LC medium the orientation dominates, but for isotropic melt the change of relaxation spectrum at superposition of steady and oscillation flows predetermines the rheological response.

Behaviour of polymer blends depends on what polymer is a matrix. If LCP, the same tendency as for pure LCP takes place: longitudinal superposition leads to decrease of complex modulus, and transversal superposition results in increase of this parameter.

For LC melts filled by carbon black the unexpected anisotropy was observed at a moderate content of the filler accompanied by decrease of viscosity compared with the neat polymer. It was explained by formation of generalised absorbed layers belonging to different particles and their stretching in the entrance zone of a capillary rheometer.

Optical interference method for liquid blend melts and dynamic mechanical spectrometry for solidified heterophase samples allow us to observe the intermediate (between two phases) layers formation with specific set of rheological properties capable to reinforce the composites. In melt state for incompatible polymers as a rule viscosity decreases but for partially compatibility the viscosity can be higher than additivity line. The essential contribution of interface slippage to increase of volume output was registered for blends of incompatible polymers. Prolonged deformation in cone-plate operating unit at moderate shear rates sometimes initiates the regular macrophase separation (formation of concentric circles enriched of one or another component).

Thus, rheology of above mentioned complex polymer systems is rather complicated and requires not only special theoretical approach, but also special equipment.

RHEOLOGICAL BEHAVIOR OF PHENOLIC-URETHANE COMPOSITION.

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Systems, constituted by phenolic resins, cured in the presence of urethane hardener were studied. The processing conditions and final physical properties of thermoset depend principally on their chemical composition, degrees of crosslinking and structure of the system. The effect of cure temperature and amount of catalyst on curing behavior were examined in this work using differential scanning calorimetry, dynamic mechanical analysis and IR-spectroscopy.

Initial parts of isothermal time dependences of viscosity can be successfully described by exponential equation: $\eta = \eta_0 \exp(k_0 t)$, where η is current viscosity, η_0 is initial viscosity, k_0 is viscosity-rate kinetic constant and t is current time. Gel-times and activation energies of curing were found by different methods. It was established that the product of the initial rate of a reaction and the gel-time is constant at various conditions of cure. In order to determine kinetic characteristics of gelation, dependences of η versus degree of conversion were plotted. The degree of conversion in the gel-point was found to be about 0,58. Time dependences of the degree of conversion (calculated from calorimetric and dynamic mechanical data) in the full range of conversions are described by first and second order kinetics. If a reaction leads to a transition to the glassy state over the course of curing first and second order equations are valid in the initial stage of the process only. The complete kinetic curve can be described by the DiBenedetto method relating shift of the T_g with the degree of conversion. Rate constant for vitrifying systems is presented as a sum of reciprocal values of chemical and diffusion constants.

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Mathematical simulation and experiments in rheology
of concentrated suspensions.

Test research of concentrated suspensions difficulties of the sizes of the dispersive phase are those of 10^{-5} - 10^{-4} m. The interpretation of the research results is blurred. And the use of many well-known methods in this case may be considered improper. However, the rheology of such systems is quite specific and characterized by quality changes of viscosity anomaly. Besides the viscosity anomaly of a regular kind one can observe dilatation, rheopexia and other typical effects along with physical experiments it is helpful to test some versions by computer analysis of the related mathematical models in order to better understand rheology of such a kind. Rheological properties of concentrated suspensions including Ni pourler in epoxy resin have been studied. These are anomaly viscous liquids, but in some cases they become dilatant, i.e. their resistance to deformation rapidly grows under shear. A system has been chosen for simulating the process, and it is a suspension including a viscous matrix and a dispersive filling made of a material with a high modulus of elasticity. The system undergoes deformation between the plane-parallel plates. The object-oriented analysis has been consistently employed. Visualness of the experiment has been provided by continuous display demonstration of the moving multiplicity of particles in the viscous medium. The effect of the concentrated filling, the deformation velocity and other parameters, upon the behavior of the model deformed has been investigated. A number of structural factors responsible for a change of mechanics of concentrated suspensions rheology and for emergence of dilatation has been observed. Good agreement of the results of mathematical and physical experiments has been discovered.

Impregnation of Fibrous Materials by Polymer Blends with Yield Stress

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Application of many advanced thermoplastics as matrices for polymer composites is restricted by very high viscosity of their melts. Blending with liquid crystal polymers (LCPs) allows to reduce viscosity and improve mechanical properties of the basic polymer. The melts of these blends demonstrate a viscoplastic behavior, that in some cases may complicate processing, particularly the impregnation of fibrous materials.

In this work we studied the rheological peculiarities of impregnation for yarns and unwoven materials made from aramide fibers by melts of liquid crystal copolyester PET and p-hydroxybenzoic acid (LCP) and its blends with aromatic polysulfone (PSF) made of biphenylolpropane and dichlorodiphenylsulfone.

We used for experiments with unwoven materials a device on the basis of capillary viscometer, and impregnation of yarns was carried out in glass capillary tubes under vacuum. Yield stress of melt was determined with help of squeezing flow technique on a high-precision DTMD linear dilatometer.

Melts of LCP and its blends with PSF demonstrate a viscoplastic behavior with maximum of yield stress for the composition 75/25 W/W. It was found that polymer blends with LCP may have a higher yield stress value in melt than that for pure LCP because of strong interphase interaction.

A new method for flow curves plotting based on impregnation kinetics was developed. The flow curves obtained from squeezing flow technique, rotational viscometry and impregnation seem to be very similar.

STRUCTURE AND PHASE TRANSITIONS IN POLY(TRIFLUOROETHOXY-CO-DODECAFLUOROETHOXY)- PHOSPHAZENES¹.

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The information about structure evolution and phase states of polymer systems for correct interpretation of rheological experiments plays an important role.

The structure and phase transitions in poly-[2,2,2-trifluoroethoxyphosphazene (PTFEP)-co-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptoxyphosphazene (DFHP)] have been studied by high temperature X-ray technique and DSC method.

It was shown that addition 0,5 - 7,5% of DFHP in the PTFEP chain leads to decrease of crystallinity degree. The meanings of interplain distances, such as d_{hko} , practically do not depend on DFHP-groups content, i.e. copolymers forms α -orthorhombic modification, inherent for PTFEP.

Copolymers containing 10 - 15% of DFHP-groups crystallize in temperature region 0 + -20° C, and when their contents is more than 15% copolymers become amorphous.

Above characteristic temperature (T_1) copolymers, with 0,5 - 5% of DFHP-groups, pass in mesophase state. After cooling from mesophase or isotropic melt copolymers as a rule crystallize in two polymorphic modification. The fraction of each of these modifications depends essentially on copolymer composition and crystallization conditions.

The temperature dependencies of interplain distances in mesophase (d_{100}^M) and average value of intermolecular distance in amorphous phase, calculated from angular position of the first amorphous halo were determined.

The values of d_{100}^M and thermal expansion coefficient $\alpha_{100} = \Delta d_{100}^M / (\Delta T \cdot d_{100}^M)$ in basic plain don't depend on DFHP-groups content, whereas the average intermolecular distance in amorphous phase increases with increase of their concentration. This fact points out that amorphous phase is enriched by DFHP-groups. Probably, it hinders to crystallization of PTFEP molecules in α -modification and decreases crystallinity degree of copolymers, as well as temperatures and enthalpies of transitions crystal-mesophase (T_1 , ΔH_1) and mesophase-isotropic melt (T_{is} , ΔH_{is}).

¹ X-ray technique research was carried out in the frame of Program "Russian Universities."

RHEOLOGICAL PROPERTIES OF MICROCRYSTALLINE CELLULOSE DISPERSIONS

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Today, microcrystalline cellulose (MCC) dispersions have become attractive owing to their increasing use in the pharmaceutical, perfumery and food industries as well as promising application as reinforcement "whiskers" in nanocomposites with a thermoplastic matrix which is a latex at the MCC introduction stage [1]. Aqueous dispersions of MCC obtained in definite conditions at the concentration $c \geq 8\%$ and room temperature are a gel with the water retention value (WRV) 300% and above.

An important condition for obtaining of a stable MCC gel is an intensive dispersion in water medium of cellulose destructed to the levelling-off degree of polymerisation (LODP) - the destructed cellulose is loaded into a vibrating or a ball mill filled in with water until a designed concentration of cellulose is reached and grinded until a gel is obtained. Dry grinding with further mixing with water, as well as dilution of the MCC concentrated paste results in the formation of a less stable gel with a lower WRV. MCC microfibrils bundle ("whiskers") dispersion with the characteristic "whiskers" sizes ≈ 30 nm and ≈ 1 μ m can be obviously obtained only by mixing with water upon the action of high shear stress. The destructed cellulose used in the present work was obtained by the thermocatalytic destruction method [2] that is preferable from the economic and ecological viewpoints, as compared to acidic hydrolysis.

The similarity of the rheological properties of MCC gels and liquid-crystalline polymers (LCP) is testified by the region of the concentrated dependence of viscosity (at low shear rates) in which the MCC dispersion viscosity becomes a decreasing function of concentration. The flow curves $\lg \eta - \lg \dot{\gamma}$ in the gel forming MCC concentration region consist, as in the case of LCP, of two pseudoplastic flow regions (at low (I) and high (III) shear rates) and a pseudo-Newtonian flow region (II), separating them. As a rule, the dynamic viscosity $|\eta^*| > \eta' > \eta''$ at $\omega = \dot{\gamma}$. The material functions $\eta(\dot{\gamma})$; $N_1(\dot{\gamma})$; $\eta'(\omega)$ and $G'(\omega)$ are satisfactorily approximated by the Akay-Leslie rheological equation of state for anisotropic viscoelastic liquids [3], modified by us, taking into account both the yield stress and the range of viscoelastic relaxation times. This enabled an adequate description of the MCC dispersions rheology peculiarities, established experimentally. The latter makes it possible to reckon them among liquid-crystalline suspensions of cellulose microfibrils.

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The Effect of Dispersic Fillers on the Creep of Polymer Composites

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Simulation of different properties of materials are extremely important in creating construction materials of polymer composites. Their fillings can be selected according to the efficiency of ones. A cheap composite can be composed by increasing the amount of the filling and having no reduction in its strength. In many composites higher energies of fracture are accompanied by increased defects, so that different relations to the fraction of the fillings are found in tension and in compression. For compression strength is more influenced by restrictions of plastic deformations of the polymer matrix and by variations of the stress-fracture propagation conditions. An evaluation of density variation of a polymer composite must include the general geometric regularities as well as the different sizes of the filling particles and the probability of their irregular spatial distribution. A study of different fillings revealed a specific feature of the epoxy matrix: the fillings are relatively more effective in composites cured at the room temperature. For polymer composites cured in conditions not necessarily leading to a high strength, the strength has a tendency of improving in the course of exploitation, therefore such composites become stronger than non-filled polymer matrices. The observation is extremely important for polymer composites intended for repair and restoration of details, whenever optimal conditions of curing are not available. The simulation of elasticity of polymer composites included also a controlled variation of the elasticity modulus of the matrix under the assumption of an absolutely rigid separated part of the matrix. The rates of creep of polymer composites, as well as the tendencies of their changes are predicted fairly well up till the 0.3 volume fraction of the filling. For larger fractions of fillings, the rates of creep increase because of the defects in the structure, which appear with the approach to the limit ratio of the filling and because of the changes in the deformation of the matrix with changes of stresses. Detailed studies suggest, that finely dispersed ceramics used as a filling of an epoxy resin, features a stable structure and does not introduce any changes in the matrix, that could lead to considerable changes of the polymer composite.

A Study of Elastic-Plastic Properties of Composites with Dispersed Fillers

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We report a study of creep and stress relaxation in a composite filled with dispersed fireclay and with foam diatomite for variable temperatures and filling concentrations.

It was found that the fireclay filling was found improves strength and especially rigidity of the composite, without changing the temperature dependence of the properties of plasticized resin. Consequently, fireclay fillers were selected in the simulation of the elastic-plastic behavior of the composites.

Creep studies of the fireclay filled composites revealed that in long term storing (4 years), their elastic-plastic behavior undergoes important changes. First, the compliance of the composites decreases, and the creep-temperature relation becomes less pronounced in the range between 293 and 333K. In spite of this, the experiments demonstrate that either long term storage or different modes of curing lead to no changes in time reduction factor $lg a_T$. In contrast to fireclay fillers, the $lg a_T$ values of composites with foam diatomite fillers do not follow exactly the prediction and depends on the filler concentration.

The elastic plastic properties of the composites were simulated by a mechanical model of consequent parallel combination of components. The possibility to use model was checked on long term loads of up to 10^8 s.

It was shown that knowing a binder creep, simple models can be used to predict composite properties after their long-term storage. However, even after additional approximation, the model gives significant deviations from the actual results for composites filled with diatomite. That is related with the effect of the filler concentration on the behavior of the epoxy binder and the influence of the temperature factor.

Rheological property of blood at myeloid growth

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The change of rheological properties of blood plays an essential role in pathogenesis of many hematological diseases. Despite universal non-specific character of hemorheological infringements, their importance in development of pathological process, the mechanisms, their causing, are various. The myeloid growth concerns to number initial-malignant paraproteinemia.

Attribute of this disease is high proliferation of one of lymphoid cells clones, in which there is the synthesis and more often secretion of paraproteins - proteins from group of immunoglobulins, having structure and basic physico - chemical and immunochemical by properties last. There are in circulation, in quantity, exceeding norm in tens of time, they promote hemorheological disturbances, changes of microcirculation, development cordial, renal and of respiratory insufficiency.

The study of hemorheology at myeloid growth shows increase of viscosity of plasma in 2 times, on occasion the viscosity of plasma raises in 4 times. The viscosity of blood, despite low hematocrit, remains at these ill in limits of physiological norm. Adsorption on a red blood cells of pathological paraproteins promote increase aggregation of erythrocytes (more, than in 2,5 times) and in a number of cases decrease of deformability of these cells. There is the increase of acidresistance of erythrocytes at relative prevalence of the highstable forms and increase of hemolytic activity of serum almost in 2 times at absence of intravessels hemolysis. Thus, myeloid growth is accompanied by expressed microhemorheologic disturbances, in mechanisms of occurrence of which the conducting role belongs to the plasma factors.

STRUCTURING AND VISCOSITY OF POLYMERIZING ORGANODISPERSIONS OF POLYACRYLATES

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The main factors affecting the structuring of polymer organodispersions as heterogeneous media are the particle size, the phase concentration, aggregative and kinetic stability of particles, the medium polarity, the nature and concentration of a diphilic stabilizer.

The process of heterophase copolymerization of acrylic monomers in organic liquid media of a different polarity has been studied.

The dispersion synthesized is particles of acrylic copolymer of tributyltinmethacrylate, methacrylamide, methacrylic acid in a precipitating organic medium. The medium is a mixture of organic liquids of a different polarity with dielectric permeability of 3-14.

As stabilizers for the particles being formed of organodispersions, the graft copolymer based on oligourethaneacrylate and block copolymer divinyl-co-styrene was used. The stabilizer possessed a diphilic nature and provided the aggregative stability of systems.

The regularities of controlling of the particle size of the dispersion phase in the course of synthesis, under conditions of a phase transition and on the storage of dispersions have been established.

The sizes of the polymer particles, depending on the medium polarity, change within 90-560 nm, those increase with decreasing the medium polarity and rising the diphilic stabilizer concentration.

With increasing the depth of the polymerizing system conversion, the size of the dispersion particles approaches a constant value at low degrees of conversion and further it does not change, whereupon the viscosity of dispersions monotonously increases till constant values.

The regions of system compositions in which viscosity properties of the dispersions obey or do not follow Einstein's law have been established.

The Effect of Dispersed Fillers on the Stress and Strain Behavior of Composites

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Dynamic solutions for composites must include the effects of their structure on the properties. Our simulation was based on the Kerner model used earlier for composites with polymer matrices. Our study covered the behavior of a complex modulus in composites "epoxy resin - metal production slag" and "epoxy resin - diatomite". Simulation of the dynamic behavior started on composites of simple structures. Such are the composites of an "elastic matrix-rigid filling". The model structure was true for models of strain. No new aspects were observed in spite of the significantly more complex strain properties for the actual part of the model in the component expressions of elastic properties of the dynamic model. The results demonstrate a specific feature of the Kerner model: the more evident expression of the matrix. The less elastic is the matrix, the relatively is the rigidity effect of the filler. The effect of the filler on the assumed part of the modulus is evident from the very close relation to the elasticity of the filler. The value of G is larger for composites with elastic fillers.

Our study of the effect of the filler showed that higher values of $\lg \sigma_k$ are found in composites more elastic fillings, although no complications were expected in our earlier analyses of the test data for polymer blends. We elaborated a model including the effects of the matrix that penetrates the pores of the filling on the dynamic behavior of composites. The computations suggest that the model does not apply to composites with certain fillings, such as cellular diatomite. Thus our further analysis covered further possible structures. As the result, we returned to structures with buffer layers among the components. A structural model of a composite with buffer layers was elaborated. With a modified description of the composite, we approached the trend noted in the tests: the values of $\lg \sigma_k$ increase for larger levels of filling. An inverse trend exists in the earlier models: the values of $\lg \sigma_k$ decrease for higher levels of filling.

We conclude from the simulation of the composite structure, that in the last the formation of the formation of the buffer layer may have an inverse effect on the dynamic behavior of the composite. The model gives a simple explanation for the damping in epoxy-resin composite with specific fillers.

Macromolecules' size determination by «turbulent viscometry» method.

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It's a well-known fact that small amounts of soluble high-polymers cause a dramatic drag reduction which appears in flow rate increase (Toms phenomenon). We assumed a viscous sublayer to consist of rolling bodies and found a relation between the flow rate increase ΔQ and a volume of macromolecular coil v_0 :

$$\Delta Q = \frac{[\eta] c}{1 + [\eta] c} \pi r^2 \tau (v_0 / \rho k T)^{1/2} \quad (1)$$

Here ΔQ is the difference between the flow rate of dilute polymer solution and the flow rate of the solvent in the same conditions; $[\eta]$ is intrinsic viscosity of the polymer; c - polymer concentration; r - radius of a tube; τ - share stress; ρ - density of the liquid; k - Boltzman's constant; T - absolute temperature. After designation of concentration-independent factors as A we get

$$\Delta Q = A \frac{[\eta] c}{1 + [\eta] c} \quad (2)$$

This equation shows that relation between ΔQ and c has a form of saturation curve. It's true for a great many experimental data. Representing (2) in the form of

$$\frac{c}{\Delta Q} = \frac{1}{[\eta] A} + \frac{1}{A} c \quad (3)$$

we get a linear function between $c/\Delta Q$ and concentration that is also confirmed experimentally. The β coefficient of this straight line looks like

$$\beta = \frac{1}{A} = \frac{1}{\pi r^2 \tau} (\rho k T / v_0)^{1/2} \quad \text{from which follows} \quad v_0 = \frac{\rho k T}{(\pi r^2 \tau \beta)^2} \quad (4)$$

The coil volume of two samples of polybutadiene in toluene calculated according to (4) were almost equal for those calculated from Flory equation.

There is a derivation of (1). The onset criterion of drag reduction, as well as influence of temperature and share stress are discussed in the frame of the model worked up. Very good compatibility of theoretical and experimental data is illustrated.

MELT RHEOLOGY, MORPHOLOGY, AND INTERFACIAL TENSION OF IMMISCIBLE POLYMER BLENDS

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For blends of polymethylmethacrylate (PMMA) and polystyrene (PS) three different aspects of melt rheology are reviewed: (A) shear oscillations, (B) shear creep and recovery, and (C) elongation and recovery:

(A) At low frequencies, the storage modulus contains a measurable portion that is due to the interfacial tension and is reflected as a separate peak in the weighted relaxation spectrum.

(B) In recovery after shear creep, a strange phenomenon is found, viz. that after a certain amount of recovery, the shear strain starts to increase again, hence, the recovery direction is reversed.

(C) These blends (8 - 40 % PS) show transient elongational melt viscosities similar to that of the PS. But their elastic recovery is different for each concentration and can reach very large values. The time scales for the viscoelastic recovery and the shape recovery (due to the interfacial tension) differ remarkably.

From the latter and the morphology the interfacial tension is determined that sufficiently coincides with the results from shear oscillations.

Blood rheology is important in pathogenesis of ischemia. If compensation of coronary, peripheral arteries occlusion is complete microcirculation depends only on pressure and viscosity of blood. In these conditions improvement of blood fluidity increases the oxygen delivery to tissues.

The aim of the study to evaluate the haemorheological status in patients with coronary and peripheral arterial occlusions and influence of plasmapheresis and lipid lowering drugs on blood rheology and clinical manifestation. We examined 396 men of middle age with peripheral atherosclerosis and 48 men with ischemic heart disease - stenocardia of III-IV functional classes. Rotational viscosimeters Rheotest-2 and AKR-2 were used for blood rheology control. In all patients viscosity of blood, plasma and serum was increased and correlated with fibrinogen, especially in near membrane layer, and red blood cells deformability in obliterans and lipid disturbances in IHD.

After plasmapheresis blood viscosity in all shear rates and plasma viscosity decreased to near control group values. Improvement of blood fluidity after 2-3 months therapy with ciprofibrate (100 mg/24 hours) confirmed the role of lipid disturbances in blood rheology. Rheological improvement was accompanied by improvement in clinics, central and peripheral hemodynamics (echocardiography and doppler evaluation).

Thus, importance of treatment of haemorheological abnormalities in patients with atherosclerotic occlusive diseases was shown.

RHEOLOGICAL APPROACH TO EVALUATION OF RESULTS OF MIXING AND GRINDING P.PH. OVCHINNIKOV

Processes of grinding and mixing are in fact simultaneous. And in both processes independent upon kind of medium of grinding and mixing there takes place variation of viscosity of medium η in function of time t and coordinates of material (physical) points of medium, that is $\eta = \eta(x(t), y(t), z(t), t)$, where $x(t)$, $y(t)$, $z(t)$ are coordinates of points. Evaluation of the process of mixing, for instance, is usually given on particular average - for instance, density, initial viscosity and so on.

«Ideal» average, that is the result or the goal of the process, is introduced. Deviations from the ideal average are formed. Variance is formed with these deviations. On the basis of variance and ideal average, which can be considered known, there is formed the integral equation, in which unknown are functions or densities of distribution which are a particular average - either density or viscosity. On the basis of the known density of distribution we find connection with the machine, which carries out the process of mixing, grinding or simultaneous process. Analytically it can be written

$$M(t) = \int_{-\infty}^{+\infty} \int \int \int_0^t \eta(x, y, z, \tau) f(x, y, z, \tau) dx dy dz d\tau = \eta_{cp}(t) \quad (1)$$

$$D(t) = \int_{-\infty}^{+\infty} \int \int \int_0^t [\eta(x, y, z, \tau) - M(t)]^2 f(x, y, z, \tau) dx dy dz d\tau, \quad (2)$$

where M , D are expectations, the variances of the process; $f(x, y, z, t)$ is density of distribution of deviations from the average. Limits of integration are found from the deviations x , y , z from X_{aver} , Y_{aver} , Z_{aver} .

In the equations (1) and (2) we may consider $M(t)$ and $D(t)$ as well as $f(x, y, z, t)$ may be interpreted as three - dimensional normal or demonstrative distribution law. Then (1) and (2) are integral equations. The process of mixing and grinding is defined by relative rate of volume component of the material rate of circulation subject to changes of rheological characteristics of the process.

MODELLING OF THE PROCESS OF A PERSON'S
ADOPTION TOWARDS THE CHANGE
OF THE SURROUNDINGS
P.PH. OVCHINNIKOV, V.A. GOLIKOV

The process of adoption is a rheological process, taking place in time, the carrier of which is a material system. For example, blood is the carrier of arterial and venous pressure. To describe the adoption of material system you should use Newton's second law or the system of these laws. In the plan of force we interpolate two forces of survival of the concrete nature: the basic force F_0 , determines the absolute level of survival, taking into consideration the previous experience of adoption of a man towards the surroundings and relative F_R , produced by a concrete nature for counteraction towards the changes of the surroundings. Consequently, let's interpolate the power influence of the surroundings towards the nature of a man – ϕ . If we suppose the adoption process, shown by any quantity (e.g. pressure, blood sedimentation rate, blood sugar level, etc.) Ψ , and the nature which is a material point of mass – m , with elastic (Gook's model) – c and viscid (Newton's model) – η characteristics you could write

$$m\ddot{\Psi} + \eta\dot{\Psi} + c\Psi = F_0 + F_R - \phi, \quad (1)$$

where «'» means the derivative on time.

If there are several characteristics of adoption process we'll get the system of appropriate equation of the type (1). The equation of the type (1) should be transferred into dimensionless equation. Let's show the quantity as

$$\Psi = \frac{\Psi_1 - \Psi_2}{\Psi_1}$$

where Ψ_1 is optimum, Ψ_2 is current. Difference characterizes the deviation. The equation (1) is transferred into dimensionless by a known way. The dimensionless right part of equation (1) is expressed by the periodical functions, the quantities of instantaneous and constant stress. According to the linearity of the equation (1) the expression for Ψ has the analogous form that is corroborated by the known experiments. Blood plays an important role in heat exchange of a man with the surroundings. The dependence of the heat transmission by blood is closely connected with the equation of blood mobility in the function from tension displacement – p .

$$E(p) \leq p[\phi_0 + (\phi_m - \phi_0) X(p)] \quad (2)$$

where $E(p)$ is a gradient, ϕ_0 , ϕ_m are the initial and finite fluidity, $X(p)$ the power of the heat transmission (wetting – sweating).

CALCULATION OF TRANSIENT VISCOELASTIC FLOWS

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This study is concerned with unsteady flow of viscoelastic fluid through a circular tube and a slightly converging channel. The rheological equation of state is represented in terms of modified integral Walters- Fredricson model including five parameters: viscosity, two relaxation times and two retardation times.

A fluid initially in its rest state is set to motion by instantaneously applied pressure gradient or volumetric flow rate. In the proposed approach to the problem solution the inertial term in the equation of motion is taken into account by averaging over the channel cross-section. For the fluid with constant viscosity we have an analytical solution in the form of series expansion. The calculations performed by the averaging method differ from the results of exact solution by 12% for the fluid velocity and by 3% for volumetric flow rate.

Depending on the ratio of relaxation to retardation times there can be a non monotonic variation of the volumetric flow rate and fluid velocity in a transient region under the action of prescribed pressure gradient. For a three -parameter model the curve of volumetric flow rate as a function of time has one extreme. The five-parameter model can give two extremes. The method of averaging acceleration over the channel cross section allows us to obtain the solution to a nonstationary problem of pseudoplastic viscoelastic flow.

DETERMINATION OF CRITICAL CONCENTRATION OF MICELLE- FORMATION OF DIPHILIC COPOLYMERS IN ORGANIC MEDIUM BY VISCOSITY METHOD

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A critical concentration of micelle-formation (CCMF) is an important characteristic of a semicolloid system. There exist a number of procedures for the determination of CCMF of surface-active substances in aqueous media.

Much less attention is paid to the study of CCMF and correspondingly of micelle-formation in non-aqueous media.

We have investigated CCMF of diphilic copolymers of block type such as block copolymer butyl rubber (co)methacrylate-butylstyrene and graft type based on oligourethaneacrylate-polystyrene in organic media of different polarity (nonane and its mixtures with methyl methacrylate).

The viscosity method of investigation was assumed as a basis and the optical methods were in possession as well.

It has been shown that a sharp change in the concentration dependence of viscosity, turbidity and the refractive index of PS and BS solutions takes place in the concentration region corresponding to CCMF. The increase in the medium polarity shifts the section of CCMF towards large concentrations of the BS and PS solutions.

The data on the CCMF study were used to elucidate the conditions of stabilization of colloid particles being formed on the dispersion polymerization. With taking into account CCMF, aggregatively stable dispersions of polymers in media of the different polarity were obtained.

Rheology-Morphology Relationships at Quouette Flow of Blends Containing LCPs.

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Polymer blends containing liquid crystalline polymers (LCPs) are enough popular objects from scientific and applied points of view. The additives of LCPs lead to essential viscosity decreasing of commercial thermoplastics and reinforcing the mechanical properties of the final products. The objects under investigation were the blends of aromatic polysulfone (PSF) and LC copolyester of polyethyleneterephthalate with p-hydroxybenzoic acid (40:60). Rheological properties of the blends were studied at Quouette flow (rheometer PIRSP, operating unite cone-plate) at 250°C. Morphology of blends was observed by optical microscopy on solidified samples after definite regime of deformation (shear rate, γ , and total deformation). For estimation of interaction between components the IR spectra were studied for blends before and after rheological tests.

PSF melt is practically Newtonian liquid, meanwhile the LCP appears viscoplastic behaviour with a tendency to yield stress existence. The main feature of these components is very high viscosity difference: LCP's viscosity is more than two decimal orders lower than PSF's viscosity. At capillary flow (high shear rates, low total deformation value) the typical for such blends behaviour takes place: non-Newtonian viscosity decreases at increase of LCP's content. Absolutely another situation was observed for Quouette-type flow. At low shear rates ($\gamma < 0.1 \text{ s}^{-1}$) the flow curve section is located near corresponding section of PSF. But at $\gamma > 0.1 \text{ s}^{-1}$ a jump of shear rate occurs at the same or even lower shear stress with transition to flow curve section inherent for pure LCP. This jump is reproducible at decrease of shear rate but at high achieved deformation only. So, depending on shear rate value one or another component of blends are responsible for their rheological behaviour.

The possible reason of such unusual shape of flow curves may be specific morphology of blend samples under deformation. At low shear rates prolonged deformation leads to regular phase separation (formation of concentric circles with different optical characteristics). IR analysis showed that neighbour circles enriched either by PSF or LCP. Besides, we can expect the specific phase separation with increase of shear rate in orthogonal direction with accumulation of one of the components near the measuring surface. It is likely LC melt, since the rheological response becomes similar to pure LCP.

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The main problem of research, to the solution of which the fulfillment of the present work, is directed consists in finding the regularities in manifestation of effects of elastic deformations when there flow solutions of polymers in conditions of a stretching hydrodynamic field, necessary for the development of ecological technology of polymeric localization of contamination areas under ground (when of poisoning and radioactive substances get in to ground waters as a result of emergencies and catastrophes), technologies to increase oil recovery of layers, and also recommendations to increase an overall performance of systems of water fire suppression and that of the device, permitting to increase flocculation ability of macromolecules at the expense of stretching hydrodynamic fields, acting on them.

Our modern ideas about orientation and deformation behaviour of macromolecules in case of a current with stretching, especially in conditions of converging current of half-diluted and moderately concentrated solutions of polymers, are far from perfection. This brings about the misunderstanding of processes, happening when pumping polymers in a layer, when submitting polymer solutions in a turbulent flow, when preparing polymeric solutions and using them as flocculants, and frequently generates a lot of misunderstanding and fallacies when interpreting experimental results. Among the attempts to explain the nature of effect Toms', lying in resistance in a friction resistance drop by the polymeric components, special place is taken by a hypothesis, based on strong deformation effect of a near-the-wall turbulence on macromolecules. For the substantiation of this hypothesis experimental proofs of presence of large degrees of deformation of macromolecules in a wall-adjacent zone of a turbulent flow are necessary. The skepticism concerning strong deformation effect of wall-adjacent turbulence on macromolecules is stipulated yet by the fact that, as a rule, shift effects wall-adjacent turbulence are analysed, and not the, jet flows ("explosions") with a longitudinal gradient of speed which arise in the wall-adjacent area. The experimental proof of macromolecular unrolling in conditions of wall-adjacent turbulence was effected in the laboratory of physics and hydrodynamics of polymer solutions (faculty of physics and ecology) of Donetsk state commercial institute (earlier Institute of soviet trade). See articles by doctor Pogrebnnyak V.G. in "The engineering and physical journal", Minsk, Belorussia, 1991, December, vol. 61, No 6, p.925-927.

The considered experimental data of polarizatin-optical study of wall turbulence of polymer solutions reducing turbulent friction give a convincing confirmation of a strong deformation effect of a hydrodynamic field on macromolecules under wall turbulence. The obtained results support the idea that the mechanism of drag reduction is uniquely related to the process of complete unrolling of macromolecules which cause nonlinear elasticity effects.

The same concerns the problem of a non-linear filtration, because filtration current can also be reduced to a superposition of two kinds of currents - those - with shift and stretching. Strong deformation effect of filtration current on molecular skeins requires yet its proof to be provided. Exhibited thus specific rheological properties of polymer solutions exhibited in this case, are stipulated by ability of macromolecules to easily change shape in a longitudinal hydrodynamic field, and this causes the change of a structure of a hydrodynamic flow (see articles by doctor V.G.Pogrebnnyak in "Polymer Science USSR", vol.34, No 3, 1992, p.270-273), and to significant physical and mechanical changes in solutions of polymers (see the article V.G.Pogrebnnyak "Dynamic structure formation in solutions hydrodynamically active polymers" // The engineering and physical journal, 1992, August, vol.63, No 2, p. 147-150).

The problems of degradation of polymer solutions get complicated by the justified supposition, contrary to a conventional point of view, that degradation is determined by initiated hydrodynamic field inside - and intermolecular bifurcations (sewings together), which predominate over a gap of macromolecular circuits.

Hence, the study of currents with stretching has the greatest value for understanding the nature of the above "anomalous" phenomena, and on the other hand - at present the orientation and deformation behaviour of macromolecules in longitudinal hydrodynamic fields is investigated very poorly and requires complex research. The work also aims at proving the hypothesis that the polymeric system - polymer - solvent in supercritical modes of current is an self-adjusting dissipative system with negative feed-backs. The obtained data about the dynamics of macromolecules in conditions of a stretching flow have also determining value for the solution of practically important problems, connected with the increase of effectiveness of fire suppression with water using polymers (for development of the device to feed of polymer into turbulent water current) and flocculation ability of macromolecules at the expense of their unrolling by a hydrodynamic field, and also for perfecting the technology of hydrocutting building materials and destruction of hard materials (mountain rocks, slags etc.) using for this purpose high-speed jets of polymer solutions.

As a result of fulfilling the work there are: investigated in details and new regularities of currents with stretching of diluted and moderately concentrated solutions was established, which are, most effective in decreasing turbulent friction and oil expulsion; there was established the physical behaviour of macromolecules in conditions of complex hydrodynamic fields (superposition of currents with stretching and shift) and reasons for increased dissipation in this case; there was studied the mechanism transition "skein - extensive circuit" and formation of supermolecular structures in solutions of polymers under the action of a hydrodynamic field in conditions of turbulent and filtration; there was clarified basic thermodynamic and mechano-chemical aspects, stipulating the degradation and dissolution rate of polymer in water, by formulating physico-chemical behaviour of macromolecules in complex hydrodynamic fields; the numerical analysis of the efflux of elastic - viscous fluid through a slot to confirm the obtained experimental data about the deformation-intense condition of macromolecules in a flow of a converging polymeric solution was executed.

The clarified main regularities of macromolecular in case behaviour of a current with a longitudinal gradient of speed and the effects of elastic deformations manifested in this case was allow to develop physico-chemical fundamentals of an ecological technology (on the basis of the polymeric water flooding method) increase oil recovery of layers; technology of polymeric localization of toxicants (including radioactive ones) under ground; structure and fundamentals of the technology of preparing rigid polymeric compositions to reduce hydrodynamic resistance of fire suppressing fluids and improving their fire suppressing properties; to investigate processes to increase flocculation properties macromolecular of polyethyleneoxyde, polyacrilamid, other polymers during clearing of polluted waters and technical oils at the expense of strong deformation effect (up to 60-90 %) hydrodynamic field on macromolecules. The work is an original research in the field of an engineering ecology and physics of polymer solutions, directed to the development of a system of views and principles, permitting to explain "anomalous" phenomena - Toms' effect, deviations from the law of Darcy, processes, connected with degradation of polymer solutions and increase of their flocculation properties, that was allow to develop physico-chemical fundamentals: an ecological technology (based on the method of polymeric water-flooding) increase oil recovery of layers; technology of polymeric localization toxicants (including radioactive ones) under ground; Structure and fundamentals of a technology of preparation of rigid polymeric compositions to reduce hydrodynamic resistance of fire-suppressing fluids and improving their fire-extinguishing properties, and also a device, permitting to increase the flocculation ability of macromolecules at the expense of their unrolling by a hydrodynamic field, by increasing thus a degree of clearing natural and waste waters and regeneration of spent lubricating oils. It was proved, that in the basis of phenomena considered in the work, there lie effects of elastic deformations which are manifested in solutions of polymers in case current with stretching.

Thus, the work demonstrates a unique approach (use of effects of elastic deformations, exhibited in solutions of polymers) for the solution of a lot of technological problems, connected with protection of environment.

The rheological investigation of fast network formed polyurethane

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To study a process of polyurethane network formation, as consequence of curing reaction of various compositions based on diphenylmethane-4,4'-diisocyanate and polyol, which were supplied by Bayer A.G., Germany, an investigation of kinetics of viscosity changes was carried out at isothermal and non-isothermal conditions.

The features of polyurethane forming are high rate of chemical transformations and significant increase of temperature as result of exothermic curing reaction. For example, even at room temperature the reaction starts practically without induction period after mixing of the initial components. The complete polyurethane solidification proceeds in 4-10 minutes and the resin temperature reaches 80-120°C for the same time.

For overcoming above mentioned difficulties the original single-screw equipment was designed and constructed for mixing and filling the neat polyurethane resin into the operating unit cone-plate of rotational rheometer. The isothermal conditions in thin gap between the cone and plate were assumed. It tooks us ~10 seconds to get homogenous mixture and ~15 seconds else to transport it into the cone-plate unit.

The same screw was used to mix the initial components directly into a barrel of capillary rheometer, where non-isothermal conditions take place. The temperature increase near the die entrance region was measured and compared with the one at adiabate conditions. Both rotational and capillary rheometers work at controlled shear rate.

It has been shown the viscosity increase rate depends on the ratio of initial components, the temperature conditions of curing and a quality of mixing. The viscosity increase depends on shear rate at rotation experiments, increasing with shear rate growth. The effect is correlated with an interface surface increase at the shear. The obtained rheokinetic curves are fitted the following equation

$$\eta = A \exp(bt),$$

where A and b are empirical constants, depend on the composition and the nature of the polyols and the isocyanates. The rate constant (b) for viscosity increase was evaluated from the slope of $\log \eta$ versus t plots at different temperatures.

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THE THEORY OF BIREFRINGENCE IN POLYMER NETWORKS WITH TOPOLOGICAL RESTRICTIONS

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A study of photoelastic properties has a great importance both for the molecular rheology of polymers and for the theory of rubber-like elasticity so far as it permits to better comprehend the structure of elastomers and processes which accompany its deformation.

The theory of birefringence in cross-linked elastomers is proposed. It is based on the model which was used early for the construction of the theory of rubber-like elasticity [1]. This model takes into account simultaneously two effects which take place at deformation and are stipulated by topological restrictions (TR): i) the infringement of deformations affinity of individual chain parts (submolecules) and ii) the change of chains fluctuation limitation in the direction normal to chain contour. The existing theories of rubber-like elasticity which are based on the concept of TR take into account, as a rule, only some one of these effects, and theories of birefringence which consider these effects are generally nonexistent.

The dependence of birefringence Δn on extention ratio λ according with proposed theory has a from:

$$\Delta n = K_1(\lambda^2 - 1/\lambda) + K_2 \Phi(\lambda, \beta)$$

where K_1 and K_2 are constants and β is the ratio of mean square chain fluctuation in the direction normal to the chain contour in an undeformed state - $\langle h^2 \rangle$ to the mean square of the chain length in a free state - NI^2 . The plot of reduced birefringence $\Delta n/2(\lambda^2 - 1/\lambda)$ vs. $1/\lambda$ is practically linear in the interval $0.25 < 1/\lambda < 0.85$ in accordance with experimental data. In so doing at small β the ratio K_2/K_1 is less than C_2/C_1 and at larger β it is on the contrary. (Here C_1 and C_2 are constants in Mooney-Rivlin equation.)

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INFLUENCE OF MOLECULAR PARAMETERS OF POLYMER FLUIDS ON THEIR NONLINEAR RHEOLOGICAL PROPERTIES

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Wording of rheological equation of state is one of the fundamental problems of the rheology and it is the basis for mathematical description of melt and solution flows of the linear polymers. Solution to this problem was obtained from microstructure notions. The properties of the polymer media were modeled by suspension nonlinear anisotropic elastic dumbbells, which do not cooperate. This permits to use the onemolecular approach for rheological equation of state, when instead of the whole totality of macromolecules only one macromolecule moving in the effective environments is considered. Presuming that the anisotropic properties of this environments are defined by average shape and orientation of themacromolecular coil, it is possible to get reserved equation for strain tensor.

Recorded rheological equation of state coincides which the basic rheological model, which was obtained earlier. And earlier the satisfactory consent of this model and experimental facts for steady shearing solution flows of a polystyrene in toluene of different molecular weights and concentrations. This is a basis for consideration of line nonlinear steady and nonsteady effects in flows of linear polymers. In this work one of the possible ways of stock-taking of polydispersion of material is realized and the dependence of steady and non-steady viscosusmetric functions from parameters of a polydispersion is reseached. Further the influence of steady shear in parallel and orthogonal directions on dinamic characteristics of a polymer system (modulus of shear and modulus of less) - is considered.

In conclusion some steady nonhomogeneous flows are considered of foundamental rheological model - the flow in infinite round tube, the flow between coaxial cylinder and the flow between parallel planes.

TO PROBLEM OF ATHEROSCLEROSIS: CHANGE OF BLOOD RHEOLOGY AND OSMOTIC RESISTANCES OF ERYTHROCYTES UNDER ACTION of FREE RADICALS

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Free radicals oxidation (FRO) is one of primary factors in the development of atherosclerosis. However action of free radicals on blood rheology are investigated unsufficiently today.

The purpose was *in vitro* research of serum oxydized components action to micro- and macrorheologic properties of blood.

Oxidation of serum have carried out under Cu^{2+} ions (1 mM/L). A degree of oxydation was characterized by equivalent quantity of malone dialdehyde (MDA, nM/mL of serum). Next serums were used (by MDA): I - $1,035 \pm 0,055$ nM/mL; II - $3,62 \pm 0,41$ nM/mL; III - $6,09 \pm 0,87$ nM/mL; IV - $8,955 \pm 0,99$ nM/mL and more.

Blood viscosity was determined by shear rates $10-300 \text{ s}^{-1}$, plasma viscosity - by shear rate 250 s^{-1} with use of rotational viscosimeter AKR-2 (Russia). Suspension stability of blood (SSB), minimal des-aggregative shear rate (MDSR, s^{-1}), τ_0 , index of erythrocytes aggregation (IEA) and index of erythrocytes deformability (IED) were calculated. Osmotic resistances of erythrocytes (ORE) was analysed too.

RESULTS. Under mild FRO activity (up to MDA $1,035 \pm 0,055$ nM/mL) IEA and IED did not change significantly. However plasma viscosity, τ_0 and SSB raised, MDSR was reduced moderately. Under raised FRO activity (MDA $3,62 \pm 0,41$ nM/mL) erythrocytes aggregation and deformability were increased but their osmotic resistance was reduced. Microrheologic changes have caused also the decrease of SSB under given degree of FRO activity. Plasma viscosity did not change. Therefore τ_0 nor was increased.

Further FRO activation was accompanied by lowered erythrocytes aggregation and their capacity to deformation. The increase of blood viscosity, τ_0 and SSB was marked also that resulting in sharp reduction of blood fluidity.

When erythrocytes were preincubed with α -Tocopherol as antioxydant there was revealed similar changes of rheologic parameters. However degree of these changes was essentially less.

Under smaller FRO activity (MDA 1,35 - 3,62 nM/mL) α -Tocopherol increased erythrocytes resistance to the action of free radicals. ORE had changes only under MDA $6,09 \pm 0,87$ nM/mL and more: sharp increase of destroyed erythrocytes count was combined with full hemolysis by NaCl 0,5-0,55%. It testified to the reduction of physiologic range for osmotic resistance of erythrocytes. Under this FRO activity hemorheologic parameters did not differ significantly between experiments with native erythrocytes and erythrocytes preincubed with α -Tocopherol.

This fact assumes extremely fast exhaustion of antioxydant reserves of blood.

CONCLUSIONS: The intensity of FRO give the expressed influence on blood rheology and osmotic resistance of erythrocytes by means of updating their structure and cells membrane charge and their environment.

Erythrocytes are steady to oxidizing stress when MDA is no more than $3,62 \pm 0,41$ nM/mL. In this range microrheologic changes are compensation but not pathology.

Erythrocytes integrates blood rheology and antioxydants system. Red blood cells are first reacting to the increase of FRO activity and there are first exhausting their compensatorial reserves.

The facts of the research confirm the rule stated by us earlier: «in blood as in suspension system the plasma is as conservative, most stable component interfering pathological changes of blood viscosity and the reduction of blood fluidity as whole».

HEMORHEOLOGIC CHARACTERISTIC OF THE PATIENTS WITH ISCHEMIC HEART DISEASE FOLLOWING TRANSMYOCARDIAL LASER REVASCULARIZATION (FIRST CLINICAL OBSERVATIONS).

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Monitoring of rheologic, coagulative immunologic examinations in 9 men aged 48-60 with sever distal lesion of the vascular bed and/or its obliteration as a result of coronary arteries occlusion, whom transmyocardial laser revascularization had been indicated based on clinical and instrumental examination, was performed. Using highly effective laser transmyocardial channels from 35 to 58 in diametr in 1mm were made on the anterior, anteriolateral, apical and posteriolateral surface of the LV wall. Increased preoperative blood viscosity at low rates deviation ($7,5 \pm 0,2$ cps), plasma viscosity ($2,1 \pm 0,02$ at N $1,7 \pm 0,01$ cps), red blood cell aggregation (aggregation ratio $1,35 \pm 0,04$ at N $1,27 \pm 0,01$ cps) were observed. High viscosity correlated with hypercoagulation syndrome, which had manifested itself by hyperfibrinogenemia ($582,2 \pm 15,9$ mg% at N230-260mg%), increased tissue factor tract activity (Quick's activity $155,4 \pm 5,4$ at N70-90%), hemostatic thrombocyte linkage activation, thrombin time reduction and adequately high neutrophilic metabolic activity ($37,5 \pm 3,1$ at N up to 14%). Red blood cell aggregation and blood viscosity decreased is observed in postoperative period (3-7 days). Plasma viscosity increases by 7 days, which may be due to the protein increase in the acute phase (fibrinogen - $744,0 \pm 18,3$ mg%, presence of fibrin-monomers++, C-reactive protein++++). Tissue factor track activity is reduced due to myocard revascularization, perfusion improvement, ischemia decrease. In this period pronounced neutrophils aggressiveness (the number of activated cells is increased up to $68,7 \pm 5,4$ %) is observed which can be due to the type of the surgical intervention. This reaction gradually weakens. There is a trend to the reduction of acute phase proteins. Coagulative and rheologic values indicate the necessity to continue and in some cases to intensify desaggregation therapy. Further observations should be directed to the matching of various schemes for desaggregation, anticoagulative, antioxidant therapy for the follow-up protocol standardisation.

RHEOLOGY AND OPTICAL ACTIVITY OF CELLULOSE ACETATES

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The rheological properties of concentrated and dilute solutions of cellulose acetates modified by vapors of those solvents which form a lyotropic LC phase with cellulose and its derivatives were studied. Earlier, vapors of such solvents had been found to strongly influence the structure of fibers and films with predominant proceeding of orientational processes [1,2]. Our study on powder samples of the polymer and the same specific solvents has shown that the process is accompanied by a change of the rheological characteristics of solutions made from the such-modified polymer. Vapors of the solvents forming a LC phase strongly influence the optical activity of the polymer as well, which is accompanied by a wide-range change of the value and even the sign of the specific optical rotation $[\alpha]$.

Our rheological studies of dilute solutions of cellulose acetates have revealed a sophisticated relation between the change of the polymer optical activity and its hydrodynamic parameters. In the case of high-concentrated solutions (25–27%) this dependence has proved to bear valuable information. A sharp correlation was observed between viscosity and specific optical rotation. Higher values of viscosity correspond to higher values of specific optical rotation in spite of the sign of $[\alpha]$. The lowest values of viscosity were observed in the range of low-angle specific rotation, $[\alpha] \rightarrow 0$ within $-10 \dots +10$ grad. Having elongated conformations with the cholesterol helix twisted at low angles, the polymer perhaps possesses the lowest resistance to flow, and, being in such a state in solution, support this orientational order due to helixization process induced by vapors of active solvents.

Fibers and fabrics made of the polymer with negative values of specific optical rotation (which is not typical for cellulose acetates in acetone) differ from ordinary acetate silk in new qualitative properties: elasticity and no "twists".

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A rheological researching of weak gels of Xanthan by transient viscometer.

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Xanthan, an exocellular polysaccharide produced by the plant pathogenic bacterium *Xanthomonas campestris* has been the subject of considerable interest in recent years because of its unusual rheological properties in solution ('weak gel') and consequent range of applications [1]. Small deformation oscillatory shear measurements have enabled a distinction to be made between so-called "strong" and "weak" gels, in particular those formed from biologically significant polysaccharides. At large deformations strong gels will rupture and fail, and will never "heal" without melting and resetting. Conversely, weak gels will recover and can flow without fracture, giving a power law response, with an exponent approaching -1, so-called "yield stress" behaviour. The rheological properties of a strong gel and a weak gel xanthan, an exocellular slime exuded by bacteria of the genus *Xanthomonas*, are measured in vitro, and related to in vivo requirements [2].

A new Couette-type viscometer has been designed to measure the flow behaviour of the gels. The outer cylinder of this device is driven by a step motor with the result that the deformation is given by a present step-by-step function. Thus, this regime of deformation of gels is a transient regime (pulsate regime). It has been found experimentally in case of the transient measurement method the rheological behaviour of the aqueous solution of Xanthan has been displayed the Newton behaviour versus the data given by a stationary method at large deformations. The "yield stress" behaviour has not been found. It is assumed that "weak" gels formed from the aqueous solution of Xanthan has been destroyed with a pulsate movement of working unit of a viscometer.

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SOME DISTINGUISHING RHEOHEMODYNAMIC FEATURES
OF THE MICROVESSELS ARTERIAL TREE.

The work is dedicated to simulation of the non-newtonian blood flow in arterial part of the microvessels system. This arterial tree is given by common knowledge of branching laws. The blood flow in every tree branch is considered quasipoiseuille approximation of blood nonlinear viscoplasticity and special concentration effects. It has been reasoned that the blood flow conditions in every branch (vessels inner radii, pressure gradients, apparent viscosities) must correspond of minimum expenditure of the pumping energy-Murray principle. There were got: pressure distributions, blood flowrates, apparent viscosities in various branches. Also were determined: quantitative estimations of the blood rheology influence on the flowrates and hemodynamic characteristics in arterial microvessels tree.

**Adhesion and Mechanical Properties of the Filled Blends of
Thermoplastics and Liquid-Crystalline Polymer**

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Adhesion of the blends of three regular thermoplastics with liquid-crystalline polymer to the aluminum and glass surface and mechanical properties of these blends filled by short fibers have been studied as a function of the blend composition. It was established that concentration dependence of adhesive strength depends on the ratios of the surface tensions of components forming the blend. Two various cases of the structure of the adhesion layer have been considered: the complete wetting of the surface by one of the blend component and incomplete wetting by both components. In the first case the interphase is formed by two layers: a first layer in direct contact with the solid surface (wetting layer) and a second layer between wetting layer and blend matrix. If adhesion between wetting layer and a matrix is lower than adhesion between solid and wetting layer, the failure of adhesion joints will take place in a zone of the contact between two components of the blend. After the phase inversion in the blend, there occurs the transition of the failure zone to the interface with solid. The transition from adhesion failure between the blend components to adhesion failure between the blend matrix and a solid is a specific feature of adhesion of two-phase blends. In the latter case the adhesion is determined by the adhesion strength of the wetting layer.

It was shown that combined application as a reinforcement of both LCP and short fibers leads to essential strengthening of thermoplastics not making worse their processability. Mechanical properties of filled blends were discussed from standpoint of peculiarities of adhesion of blends to the solid surface.

Rheological Properties of Superplastic Materials Affected by Structural Dynamics

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Various kinds of superplasticity, i.e. fine structure superplasticity (FSSP), high strain rate superplasticity (HSRSP) and phase transformation superplasticity (PTSP) as well as superplastic-like behaviour of some natural and industrial materials evidently belong to the same type of rheological behaviour which can be defined as non-linear viscoplastic flow. A phenomenological model has been developed to describe deformation of polycrystalline materials at elevated temperatures in a wide range of strain rates with respect to structure evolution during deformation. There is a positive experience in using this model for computer simulation of various processes of isothermal superplastic forming. There are at least two advantages of this model as compared with other models: 1) structure evolution during SPD process is possible to be taken into account; 2) rheological parameters of the model are independent on strain rate, so the model works perfectly in any point of deformation zone which in most cases is known to be very inhomogeneous in strain rates.

Rheological analysis of FSSP, HSRSP and PTSP materials along with a slurry during rheocasting shows similarities and peculiarities of superplastic and superplastic-like behaviour. The value of apparent viscosity seems to be an informative index for estimation of rheological and physical state of grain boundaries as a viscous phase and of polycrystalline material as a whole. A new process of impulse bulk forming is presented to show unique possibility of joining in one process two stages of a regular superplastic technology, i.e. preparation of ultra-fine grain structure followed by HSRSP deformation.

Modelling of local dynamics and viscoelastic relaxation of the elastomer networks with different energies of junctions

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Since 71th when reptation model was proposed by De Gennes¹ and then developed by Doi and Edwards² this theory had a remarkable success and nowadays it is a conventional point of view on the long-time polymer dynamic behaviour. But along with ordinary linear polymers there is still a broad class of polymers such as copolymers, ionomers, biopolymeric gels which properties, especially on the long-time scale, substantially differ from ones of common polymers. Do we need a new theory for ascribing such systems and are there any evidences of being entanglements not only geometrical obstacles?

In the present work we have provided some molecular dynamic simulations of the local dynamics of intermolecular couplings on the models of copolymers and network polymers. The question of interest was: at what extent may high-energy intermolecular bonds constrain mobility of low-energy intermolecular bonds. Comparison was drawn with NMR ¹³C data. Also on the basis of the earlier developed theoretical model³ was provided numerical investigation of viscoelastic behaviour of the elastomer network with physical junctions. The scope of thermodynamical parameters of junctions, such as concentration, energy and entropy at which anomalous strain behaviour occurs was defined. The results was compared with stress-strain curves of butadiene-nitrile network copolymers at temperature region 20...100°C and strain velocity 0.5...500 mm/min.

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Blood rheology in diabetes mellitus and necessity of their specific correction.

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Haemorheology disorders (HrD) can be one of the first symptoms of development and/or of decompensation of the diabetes mellitus (DM). Most significant parameters of blood viscosity in DM patients are red cell aggregate capacity and deformability, hematokrit, plasma viscosity, and fluidity threshold, Kesson viscosity, and platelet aggregate capacity.

Parameters of blood viscosity (red cell aggregate capacity and velocity, hematokrit, fluidity threshold, Kesson viscosity) were studied in 326 DM patients. We found that hemorheologic deterioration is typical for DM. DM is an significant independent risk factor of HrD. All parameters of haemorheology (Hr) are substantially altered in most DM patients. Hr is obligatory deteriorated during DM decompensation. HrD may be found already at moment when DM is detected for the first time. There is no correlation of Hr parameters with age and disease duration in DM, but there are significant correlations with gender (Hr worsen in males), presence of DM complications (retinopathy II-III, nephropathy IV-V and renal failure, cerebrovascular disease, distal polyneuropathy) and concomitant diseases (obesity, coronary artery disease, hypertension, congestive heart failure, cerebral insult).

We believe special correction of blood rheology in DM to be one of the basic principles of management of such patients. Hr correction must be complex, prolonged and begins as early as possible. The main directions of HrD correction are: DM compensation; pharmacological and (if necessary) extracorporal correction of hematokrit, red cells and platelet aggregation, plasma viscosity; elimination of the most important pathogenic factors of HrD. There was significant improvement of Hr parameters after DM compensation was reached. We found that plasmapheresis (PA) is the most potent method for correction of Hr in DM patients. All studied parameters were significantly improved after PA course. Some drugs (pentoxiphylline, tanacan, alisat) have beneficial effect on Hr in our study. We have detected no effect of four week course of α -tocoferol on blood viscosity parameters in MD patients.

Urgent Problems of Mathematical Modeling of High-Temperature Deformation of Powder Materials

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Methodology of mathematical modeling for the processes of SHS compaction, extrusion and disintegration is discussed. A review of results on mathematical modeling of rheodynamics and heat transfer of a composite materials under their compacting, extruding and disintegrating has been presented. These materials are characterised by a high initial porosity (of up to 50%), and they behave as high-viscous liquids (viscosity is from 10 to 10 Pa s) in the temperature region of their processing (2000-3000 K).

To describe the flow of such materials under their deformation the system of equations of continuity, motion, heat conductance and the rheological equations is employed. The model takes into account the initial density distribution throughout the material. Determination of parameters areas at which the different regimes of above mentioned processes are carried out is the main result of mathematical modeling of these processes.

Some problems of mathematical modeling concerning the mutually proceeding processes of structure formation and rheodynamics are considered.

Rheological Characteristics of Carbide and Boride of SHS Materials

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A novel process, called mould free SHS - compression, for compressing materials at constant force is proposed. The essence of the technique consists in compacting of combustion products with unreasonable pressure (from 10 to 200 Mpa). The advantages of this technique are the use of the favourable strain distribution and shear plastic deformation of the material. They are contributory factors for cracks and voids in the material under deformation have been "healed". The study by means this technique concerns itself with the peculiarities of rheological behaviour of the materials based on titanium carbide and titanium boride with nickel binder.

For the ability of the material to plastic deformation we have proposed to use a geometric parameter having the meaning of the ratio of the initial sample area to final one. Dependence of that parameter on the metal binder quantity, its chemical composition and initial sample height has been studied. Homogenous character of these dependencies which was due to concurrent action of heat evolution and liquid phase has been studied. The ability of material to plastic deformation depends not only on the quantity of liquid phase, but on plasticity of metal binder, the possibility for intermetalides formations, the solubility of boron and carbon in molten metal binder as well.

Methods of Rheometry for SHS Materials

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The concepts of the ability of different composite refractory materials to plastic deformation and of various modes of deformations are formulated. Specific structure features of SHS materials as the objects of rheology are discussed, various types of viscosimetric flows and the choices of rheological variables are delineated. Such factors as nonuniformity of the porosity distribution, external friction and nonisothermality of the process are considered.

Direct and inverse problems of rheology are considered. A compression rheometer intended for studying the compaction kinetics and rheological properties of SHS materials is described. The data on the rheological properties of the material based on molybdenum disilicide are represented. Some methods of approximate estimates of viscosity coefficients are discussed.

CORRELATION OF RHEOLOGICAL AND SURFACE PROPERTIES FOR POLYACRYLAMIDE SOLUTIONS AND GELS

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Water soluble polymers are employed in various processes of oil production and transportation. Due to their unique rheological properties viscoelastic gels are widely used in pipe-line transport of oil and oil products. They serve as mobile phase separators and cleaners.

The study of surface properties of polyacrylamide (PAA) solutions and gels and their correlation with those of a polymer body, which is used in industry, are of prime importance for scientific substantiation and for the improvement of such solutions and gels for pipe-line transport.

Surface phenomena are closely connected with those proceeding in the bulk. As a result the changes in the interface conditions initiate the changes in the bulk and vice versa.

The relation between rheological characteristics and surface properties has been studied for PAA solutions and gels. The rheological properties of the prepared solutions and gels were studied by capillary, rotary and low-frequency vibration viscosimetry. The surface properties were studied by a stalagmometric method, wetting angles and adhesion. Using these methods we studied the changes in viscosity and elasticity, measured wetting angles and adhesion under temperature-time dependence.

Using viscosimetry it has been shown that at a concentration below a critical point, when a physical network of engagement is formed mainly due to Van der Waals forces, the surface properties have minimum values. A sharp increase is observed with a rise of this concentration.

Using correlation of surface and rheological characteristics for PAA solutions and gels, temperature-time dependence and the elements of diffusion approach to adhesion phenomena one can explain the nature of adhesion appearance in PAA solutions and gels and thereby predict important technological properties.

RHEOLOGIC PROPERTIES OF MELTS AND STRUCTURE FORMATION PROCESSES IN TERNARY POLYMER MELTS

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The influence of low-molecular and oligomeric additives on flow regularities and structure formation processes within polypropylene - co-polyamide (PP/CPA) and polyoximethylene - co-polyamide (POM/CPA) was investigated. Such additives as sodium oleate, sodium chloride and polymethylsiloxane were used. All substances investigated are polar and they demonstrate specific interactions with matrix component (CPA) at the interphase. Infrared spectra have confirmed the dipole-dipole and ion-dipole interactions between an additive and CPA macromolecules. Occurrence of so strong specific interactions alters macro- and microrheologic processes in flow of ternary mixture melts. So, when 0.5 % to 3.0 % of low-molecular additive (sodium oleate) are introduced, the PP/CPA mixture melts' viscosity and elasticity are increased. Micro-rheologic studies have confirmed the dispersive influence of sodium oleate on polymer's dispersion phase and increase of kinetic stability of binary mixture melt. Liquid streams of polymer's dispersion phase that were emerged, possess the long lifetime if there is an additive, as compared to that lifetime in binary mixture melt. Due to the above-mentioned micro-rheologic processes the structure formation in ternary polymer mixtures is improved: the prevailing structure type are microfibrils of continuous length, their average diameter and distribution dispersion by diameter values are decreased.

Therefore, the above-mentioned additives allow to regulate the structure formation processes via alteration of micro-rheologic phenomena at the component interphase.

RHEOLOGY AND THE STABILITY OF CONCENTRATED DISPERSIONS WITH
DUE ACCOUNT OF THE DYNAMICS OF CONTACT INTERACTIONS

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A theory of the complete rheological flow curve has been developed while taking into account the mechanism of the formation of continuity ruptures in structure, its breaking up into aggregates, and their formation as a result of the overcoming of repulsion forces under the conditions of inertial coagulation. The regularities of the loss of sedimentational stability by the system are considered in relation to those processes. A theory of the sedimentation stability of structured dispersions in flow has been developed while taking into account the aggregate mechanism of destruction of the structure depending on the deformation rate. An analysis has been presented of the dilatant properties of dispersions at different concentrations of the disperse phase. The theory relating the rheological properties with the aggregative and the sedimentational stability of disperse systems has been experimentally substantiated by the use of model systems representing suspensions of monodisperse spherical particles in polar and nonpolar media within a wide range of dispersity values (diameter of the particles from 70 Å to 1500 Å) and concentrations (from 2.5% - fractile systems - to 70% - compact filled dispersions). The experimental verification has been carried out both for the case of dispersions with strong (lyophobic) interactions between the particles of disperse phases (so-called close-range coagulation) and for that of the systems containing the particles stabilized by different kinds of surfactants (e.g. the weak coagulation contacts - so-called long-range coagulation). The computer modelling of the behaviour of structured dispersions in the shear flow and under the effect of a vibration field has been carried out both for the structured dispersions as formed by the fractile aggregates, and for highly-filled systems. The results of this modelling are illustrated by a computer film generalizing the rheological properties of the systems in the shear flow and under vibration, and the mechanism of the breaking up and formations of their structure.

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MICROPHASE EQUILIBRIA AND RHEOLOGY IN THE COMPOSITIONS
OF CRYSTALLIZABLE SEGMENTED POLYURETHANE (PU)-
POLYACRYLATE (PA) -DMF

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By studying with rheological methods, phase and microphase separation in the solution of crystallizable segmented polyurethanes (PU_s) were investigated on the ternary system PU_s - polyacrylate (PA) - dimethyl formamide (DMF). PU_s synthesized on the basis of polyethyleneglycoladipate, 4,4-diphenylmethanediisocyanate and 1,4-butanediol have been studied. The molecular weights of both soft (flexible) and rigid block PU_s segments were about 2000. PMMA (MM 95 000; 150 000; 270 000; 370 000) and copolymers MMA with BA (MM 95 000) containing 5 and 10% of BA were used as polymer selective interacting with the flexible block PU_s .

Effects of specific interactions of PA with the flexible block on the conformational state of macromolecules PU_s were studied by rheological and structural-morphological methods for concentration solutions and by capillary viscosimetry in the region of dilute solutions. The experimentally obtained constants of the interaction of components of the ternary system were compared. The calculated solubility parameters components were compared with experimental values.

It has been found out that the BA content increase in copolymers led up to a significant conformational reconstruction of the PU_s macromolecules, and a growth the region of microphase formations. However, effects of MM PMMA have been insignificant.

By studying with microinterferent method on the system PMMA and polyethyleneglycoladipate (MM 2000), it has been confirmed possibility of complete combination flexible block and PA.

It has been established that the level of separation in the segmented PU_s can be varied by controlling the relationship between the specific polymers, there by changing the structure and tensile strength properties of the former.

THE RHEOLOGICAL FACTOR IN POLYMER COMPOSITIONS PROCESSING.

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To estimate and forecast technological properties of rubber blend mostly Mooney viscosity and plasticity data are used. But plasticity does not display real processing conditions, because is measured when rate of deformation is low. The most convenient for researching of polymer compositions processing is method of capillary viscometry. Modern instruments, such as automatic viscometer "Monsanto" allow to create shear action over the range 1-5000 1/s, overlapping the conditions of processing practically on every type of polymer processing equipment. Curves of flow give necessary information for estimation and forecast polymer compositions behaviour during process.

Using capillary viscometry, the influence of rheological factors on processing of extended rubber, based on cis-polyisoprene, is considered. We showed that specificity of cis-polyisoprene based blends processing is conditioned by crystallisation of rubber under shearing strain, while shearing strain depends on conditions of processing, fillers and elastomere molecular characteristics. This process is sharply monitored on dependencies of stress versus rate of share, conformed to the conditions of processing and allows to compare and forecast technological behaviour of compositions, obtained in laboratory and real production conditions.

RHEOLOGIC PROPERTIES OF BLOOD IN PATIENTS WITH UNSTABLE ANGINA.

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We studied blood viscosity, aggregation and deformability of erythrocytes, platelet aggregation in patients with unstable angina and interconnection among above mentioned indices. 102 patients and 38 healthy, people of the similar age were examined.

We revealed statistically higher indices of blood viscosity ($p<0,02$) and aggregation of erythrocytes ($p<0,05$), higher rate and degree of aggregation of platelets ($p<0,001$), but lower indices of deformability of erythrocytes ($p<0,05$) in patients compared to the group of healthy people.

Positive correlation between aggregation of platelets and erythrocytes ($r=0,72$) was found out.

Higher indices of blood viscosity and aggregation of erythrocytes are the reasons for disturbances of haemorheology in patients with unstable angina. Besides, when blood viscosity is high, platelet aggregation becomes more intensive.

BASIC FLOWS OF GENERALIZED SECOND GRADE FLUIDS

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Presently there exist several new developments in fluid mechanics that are concerned with structures within the fluids. Certain fluids, e.g., emulsions, solutions of polymers, polymer melts and suspensions are known to fall beyond the domain of applications of the classical theory of Newtonian fluids.

Several constitutive relations are used to model the non-Newtonian characteristics exhibited by some fluids. Integral models, which take the past history of deformation into account, are to be used if memory effects are important. However, for many fluids, only a very short part of the history of the deformations has an influence on the stress. The constitutive relations for these fluids may be expressed as functions of the deformation gradient and its derivatives evaluated at the current time. A material in which the stress depends only on a finite number of these time derivatives is called a material of the differential type. The stress in a fluid of differential type of complexity j depends on the velocity gradient and its first $(j-1)$ derivatives.

As a non-Newtonian fluid model of differential type, the second grade fluid of Rivlin-Ericksen is extensively used by both theorists and experimenters. The constitutive relation for this viscoelastic fluid is given as follows:

$$\mathbf{T} = -p\mathbf{I} + \mu\mathbf{A}_1 + \alpha_1\mathbf{A}_1^2 + \beta\mathbf{A}_2$$

where p is the pressure, μ is the viscosity, α_1 , α_2 are the material moduli. \mathbf{A}_1 and \mathbf{A}_2 are the first two Rivlin-Ericksen tensors defined by:

$$\mathbf{A}_1 = \mathbf{L} + \mathbf{L}^T, \quad \mathbf{A}_2 = \dot{\mathbf{A}}_1 + \mathbf{A}_1\mathbf{L} + \mathbf{L}^T\mathbf{A}_1, \quad \mathbf{L} = \text{grad } \mathbf{v},$$

where \mathbf{v} is the velocity vector and $(\dot{})$ represents the material derivative with respect to time.

Many fluids of engineering interest appear to exhibit yield behaviour, where flow occurs only when the imposed stress exceeds a critical yield stress. To describe the rheological behaviour of such viscoplastic fluids the non-linear model of Shulman may be used:

$$\mathbf{T} = -p\mathbf{I} + M\mathbf{A}_1, \quad M = \left[\frac{\tau_0}{\mu} + \left(\frac{\mu}{A} \right)^{\frac{1}{m}} \right] A^{-1}, \quad A = \left[\frac{1}{2} \text{tr}(\mathbf{A}_1^2) \right]^{\frac{1}{2}},$$

where τ_0 is the yield shear stress, μ is now the coefficient of plastic viscosity, m and n are non-linearity indices, A is the second invariant of the stretching tensor. By reducing the coefficients in the Shulman equation one can obtain simpler models describing the flow of viscoplastic fluid.

To obtain a model that does exhibit both viscoplastic and viscoelastic behaviour we propose the following two constitutive equations:

– model I: $\mathbf{T} = -p\mathbf{I} + M\mathbf{A}_1 + \alpha^{(1)}\mathbf{A}_1^2 + \beta^{(1)}\mathbf{A}_2, \quad \alpha^{(1)} = \alpha, \quad \beta^{(1)} = \beta;$

– model II: $\mathbf{T} = -p\mathbf{I} + M(\mathbf{A}_1 + \alpha^{(2)}\mathbf{A}_1^2 + \beta^{(2)}\mathbf{A}_2).$

In this case, when $\alpha^{(1)} = \beta^{(1)} = 0$, both models reduced to the Shulman model and when $\tau_0 = 0$, $m = n = 1$, both models become the model for the fluid of second grade. It should be remarked that both the models (I) and (II) are special cases of fluids of complexity 2.

The aim of this paper is a study of basic flows of generalized second grade fluids given here as model I or model II in simple geometries of engineering interest.

Rheology of Superplastic Ceramics

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In terms of rheology, superplastic materials belong to a class of viscoplastic media with great contribution of viscous behavior and are generally associated with fine-grained structure. Modern ceramics with submicron grain size are able to exhibit superplasticity during high-temperature deformation. This paper reviews some of recent researches on rheological behavior of fine-grained yttria-stabilized tetragonal zirconia. Stress, strain and strain rate relationships as well as their dependencies on temperature and grain size have been analyzed. Structural kinetic processes (dynamic grain growth and evolution of porosity) as functions of temperature and deformation parameters have been considered. Constitutive equation of classic rheology describing a phenomenology of superplastic deformation as functional correlation between tensor components of stress and strain rate has been analyzed for the case of superplastic ceramic flow. Rheological properties of a material are taken into account by means of scalar rheological coefficient of apparent viscosity which is a function of temperature, effective stress (or strain rate) and structure state of the material. An approach based on viscosity analysis of independent and bounded processes on different structural levels has been developed. An assumption of two deformation mechanisms, i.e. grain boundary sliding and intragranular creep, has been proposed for description of superplastic deformation. It is shown that both these mechanisms are independent contributors into the total deformation of fine-grained ceramic. Further analysis is made to define deformation mechanisms that accommodate grain boundary sliding and intragranular creep. Grain boundary diffusion and evolution of porosity are considered to be possible accommodation mechanisms. A peculiarities of structure have been studied on the base of microrheological analysis of dispersed system "viscoplastic grain nucleus - fluid-like grain boundary".

STRUCTURIZATION IN OIL DISPERSED SYSTEMS
AND ANOMALY OF THEIR RHEOLOGICAL PROPERTIES

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The mechanisms of structurization occurring in oil dispersed systems (ODS) have been determined based on numerous studies on chemical and structural-group compositions of oils. They are different for high-paraffin and high-resin oils. On the other hand, it has been shown that it is impossible to understand the nature of these phenomena without taking into account intermolecular interactions causing structurization and anomaly of rheological properties. At present the formation of associative combinations of spherical symmetric shape in ODS has been proved to result from interactions of quantum character between paramagnetic molecules or between paramagnetic and diamagnetic molecules. This approach explains many aspects of anomalous rheological behaviour of oils.

Viscosity-temperature relations in the oils under study are quite different. It is an evidence of different types of structurization occurring in oils. The changes in structural-mechanical characteristics are immediately connected with reactivity of oil systems. It was determined based on the data used to define acceptors of peroxyradicals (APR) and paramagnetic sites. The calculated values of activation heats for viscous flow indicate that homolytic processes are the most possible ones in ODS to form associates, the structural fragments of which are biradical in character.

Polyextremal change of rheological properties caused by external factors (additives, temperature and magnetic fields) is a specific feature of ODS behaviour. Thermodynamic instability of oil systems is also realized in a change of rheological characteristics in the course of time. The results of APS determination show that such an anomalous behaviour of oils is independent of a number of stable radicals and is defined by their reactivity. Additives, physical fields and time factor affect the formation, recombination and destruction of associative combinations.

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